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**HALOCARBONS AS HALON
REPLACEMENTS: PHASE II -
LABORATORY TESTING OF HALON
1301 REPLACEMENTS**

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13. ABSTRACT (Maximum 200 words) As a result of stratospheric ozone depletion and greenhouse warming concerns, the present halon fire-extinguishing agents will be phased out by 1 January 1994 under an international treaty. The U.S. Air Force has placed a high priority on the development of substitute agents to replace halon fire suppressants. This report describes the laboratory-scale experimental work performed on the Halon 1301 replacement agents. The 5/8-scale NMERI cup burner was used extensively throughout this program. A new laboratory total-flood test apparatus—the Laboratory Extinguishment and Emissions Test Chamber (LEETC)—has been constructed to allow both determination of extinguishment concentrations under a total-flood scenario and to measure emissions. Emissions were determined using the Fourier transform infrared (FTIR) spectrometer. The LEETC provided extremely valuable information on both extinguishment and on agent decomposition products under total-flood conditions. The cup-burner results showed that no first-generation agent (hydrochlorofluorocarbon, hydrofluorocarbon, or perfluorocarbon) will provide extinguishment equivalent to that obtained with the present halons. It is recommended that investigations of second-generation Halon 1301 replacement agents be initiated. These agents contain bromine and/or iodine, but have low ozone-depletion potentials and low atmospheric lifetimes because of tropospheric degradation. Further work to develop refined equipment, techniques, and test protocols is also recommended.				
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EXECUTIVE SUMMARY

A. OBJECTIVE

The objective of the overall effort is to develop one or more replacement clean, halocarbon fire-extinguishing streaming agents to substitute for Halons 1211 and 1301. The goal of this portion of the Phase II effort was to develop laboratory-scale testing procedures and test selected agents that could serve as total-flood replacements for Halon 1301.

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B. BACKGROUND

Halon firefighting agents have been used for many years. Because of their combination of effectiveness, cleanliness, safety, and relatively low cost, little incentive has been given in the past to develop new chemicals. Since the 1980s, however, concerns about the environmental impact of halons has been increasing. Calculations and experimental data indicate that halons deplete stratospheric ozone more severely, on a per-pound basis, than do chlorofluorocarbons (CFCs). The dangers to the atmosphere posed by CFCs, halons, and other volatile halocarbons through stratospheric ozone depletion and global warming are becoming increasingly evident. As a result of these concerns, the present halon fire-extinguishing agents will be phased out by 1 Jan 1994, under an international treaty. The United States Air Force has placed a high priority on the development of substitute agents to replace halon fire suppressants.

In Phase I of this project, all information collected during the previous work was reviewed and updated, and experimental plans were prepared. The Phase I efforts for Halon 1211¹ and Halon 1301² replacements are documented in separate reports.

¹ Nimitz, J. S., Tapscott, R. E., Skaggs, S. R., and Moore, T. A., *Halocarbons as Halon Replacements: Technology Review and Initiation*, ESL-TR-90-38, Vol. 1 of 5, AFESC, Tyndall AFB, FL, March 1991.

² Tapscott, R. E., Dierdorf, D. S., Moore, T. A., and Skaggs, S. R., *Halocarbons as Halon Replacements: Phase I - Technology Review and Initiation, Halon 1301 Replacements*, ESL-TR-90-38, Vol. 2 of 5, WL, Tyndall AFB, FL, March 1993.

C. SCOPE

The scope of the overall task involves the development of one or more halocarbon replacements for Halons 1211 and 1301. The target criteria³ for the replacement agents are (1) the agent leaves no residue upon evaporation; (2) the ODP (ozone-depletion potential) is 0.05 or less on either a per-molecule basis or a unit-weight basis when compared with CFC-11; (3) the estimated or reported acute toxicity is equal to or better than that of the halon being replaced; (4) other environmental impacts are equal to or less than that of the halon being replaced; and (5) no major changes in Air Force equipment are required for storage, transfer, or delivery.

This report covers the laboratory-scale experimental work performed on the Halon 1301 replacement agents only. Note, however, that many of the agents studied could be used for replacement of either Halon 1301 or Halon 1211.

D. METHODOLOGY

Laboratory-scale testing using tests appropriate to total-flood agents was established, and extinguishment concentrations were determined. In addition, preliminary measurements on emissions were carried out. Such emissions testing is considered important since all, or nearly all, of the first-generation candidate total-flood agents yield increased amounts of toxic decomposition products.

E. TEST DESCRIPTION

The 5/8-scale NMERI (New Mexico Engineering Research Institute) cup burner was used extensively throughout this program.⁴ A new laboratory total-flood test

³ Tapscott, R. E., Nimitz, J. S., Skaggs, S. R., Walters, E. A., and Arneberg, D. L., *Halocarbons as Halon Replacements: Phase II—Laboratory Testing, Halon 1211 Replacements*, ESL-TR-90-38, Vol. 3 of 5, WL, Tyndall AFB, FL, March 1993.

⁴ Moore, T. A., Moore, J. P., Nimitz, J. S., Lee, M.E., Beeson, J. D., and Tapscott, R. E., *Alternative Training Agents, Phase II—Laboratory Scale Experimental Work*, ESL-TR-90-39, Vol. 2 of 4, Air Force Engineering and Services Center, Tyndall AFB, FL, August 1990.

apparatus—the Laboratory Extinguishment and Emissions Test Chamber (LEETC)—has been constructed to allow determination of both extinguishment concentrations and emissions under a total-flood scenario. Emissions were determined using a Fourier transform infrared (FTIR) spectrometer.

F. RESULTS

Cup-burner extinguishment concentrations have now been determined for 61 halocarbon compounds. Preliminary test results for both emissions and extinguishment have been obtained using the LEETC.

G. CONCLUSIONS

The testing confirms that the LEETC provides valuable information on both extinguishment and agent decomposition products under total-flood conditions. The cup-burner results show that no first-generation (hydrochlorofluorocarbon, hydrofluorocarbon, or perfluorocarbon) agent will provide extinguishment efficiencies equivalent to those obtained with the present halons. The LEETC method was validated and no specific agent performance characteristics were shown by the method at this time.

H. RECOMMENDATIONS

It is recommended that investigations of second-generation Halon 1301 replacement agents be initiated. These agents contain bromine and/or iodine but have low ozone-depletion potentials and low atmospheric lifetimes because of tropospheric degradation.

It is also recommended that work be performed to develop refined equipment and techniques for full utilization of the equipment developed during this work. In particular, cup-burner methodologies and/or equipment to permit facile determinations of extinguishment concentrations for agents with boiling points near room temperature

equivalent to those obtained with the present halons. The LEETC method was validated and no specific agent performance characteristics were shown by the method at this time.


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It is also recommended that work be performed to develop refined equipment and techniques for full utilization of the equipment developed during this work. In particular, cup-burner methodologies and/or equipment to permit facile determinations of extinguishment concentrations for agents with boiling points near room temperature are needed. Data on cup-burner extinguishment concentrations relative to fuels other than *n*-heptane are needed. A method for selecting pool fire sizes that allows scaling of emission studies as a function of chamber size is required. Work to develop a good laboratory-scale test for total-flood agents in Class A fires of cellulosic materials should be continued. At present, only expensive, wood crib fire tests are used to determine Class A performance, and these tests may not accurately represent the types of Class A fire scenarios likely to be encountered.

PREFACE

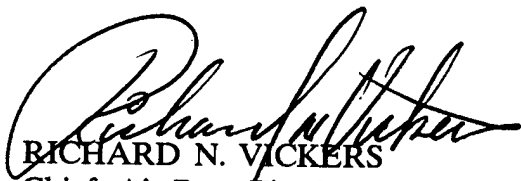
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LIST OF ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing and Materials
CAS	Chemical Abstract Service
CFCs	Chlorofluorocarbons
cm	Centimeter
cm ⁻¹	Reciprocal centimeters (wave numbers)
FC	(Per)fluorocarbon
FTIR	Fourier transform infrared
HCFC	Hydrochlorocarbon
HFC	Hydrofluorocarbon
ICI	Imperial Chemical Industries
IR	Infrared
LEETC	Laboratory Extinguishment and Emissions Test Chamber
MCSA	Mid-chamber sample area
MCT	Mercury, cadmium, tellurium
MFLOPS	Million floating point operations per second
μm	Micrometer
mL	Milliliter
min	Minute
MS-DOS	Microsoft Disk Operating System
NFPA	National Fire Protection Association
NMERI	New Mexico Engineering Research Laboratory
NRL	Naval Research Laboratory
NTIS	National Technical Information Service
PFC	Perfluorocarbon
ppm	Parts per million
QSAR	Quantitative structure activity relationship
TRIR	Time-resolved infrared

SECTION I

INTRODUCTION

A. OBJECTIVE

The objective of the overall effort is to develop one or more alternative clean halocarbon fire-extinguishing streaming agents to replace Halons 1211 and 1301. The goal of this Phase II effort was to develop laboratory-scale testing procedures and test selected agents that could serve as total-flood replacements for Halon 1301.

B. BACKGROUND

Work performed under the Air Force project, "Next-Generation Fire Extinguishing Agent," laid a foundation for the development of new firefighting agents. In Phase I of that project, the theory and technology of fire suppression were reviewed and used to establish directions for continuing agent development (Reference 1). In Phase II, selected laboratory experiments on replacement agents were performed (Reference 2). Phase III initiated work on a training agent replacement (Reference 3), and Phase IV provided additional test data on replacement training agents (Reference 4). The purpose of Phases III and V was to determine whether the development of replacements for training agents was a viable option and to find the most promising directed approach in such an effort. Phase V of "Next-Generation Fire Extinguishing Agents" supplied the initial versions of needed databases on candidate agents for use in both training and general firefighting (Reference 5). These databases included information on ozone depletion, toxicity, physical properties, and availability. Ozone-depletion potential (ODP) and fire suppression prediction methodologies were also proposed, and construction of a literature database was initiated.

Based on the results of the Phase V effort, two independent projects were initiated. "Alternative Training Agents" was directed toward development of a halon replacement for firefighter training only. "Halocarbons as Halon Replacements" was directed toward development of general-purpose halon replacement agents.

"Alternative Training Agents" had four phases. Phase I included a technology review and developed methodologies for predicting agent properties (Reference 6). Laboratory- and medium-scale experimental studies were carried out in Phases II and III (References 7 and 8). The final agents selected (HCFC-123 and blends) were validated in Phase IV (Reference 9).

"Halocarbons as Halon Replacements," was initially directed only toward a Halon 1211 replacement; however, the project was later amended to include replacement of Halon 1301. As amended, the subtask requires separate reports for the Halon 1211 and Halon 1301 efforts in each of three phases; however, owing to decreases in Air Force resources, Phase III work on Halon 1301 replacements was discontinued at the request of the Air Force. The Phase I effort applicable to Halon 1301 replacements is documented in Reference 10. The present report covers the Phase II effort on Halon 1301 replacements. Criteria for selection of Halon 1301 replacements are discussed in Reference 10.

C. REQUIREMENTS

The requirements for the Phase II effort on Halon 1301 replacements are as follows:

1. The necessary laboratory facilities to conduct fire suppression tests were to be established. The testing was to include tests indicative of agent performance under total-flood conditions.
2. As candidate materials were obtained or prepared, their extinguishment characteristics were to be determined. Other properties could be determined in the laboratory as required for estimation of agent performance under real-fire conditions and to assess the candidate's ability to meet targeted criteria. An enhanced flame extinguishment algorithm, based on correlation with a broader baseline of rigorous calculations, including a statistical sampling of brominated candidates, was to be

developed. Numerous toxicity issues are emerging in regulatory discussions, generating the need for more expansive QSAR development actions. Further QSAR development and validation were to include a corresponding level of laboratory testing as needed.

3. The results of the extinguishment tests were to be used to improve the fire suppression estimation methods reviewed and developed in Phase I. Specific test series could be set up to develop needed data for these estimation methodologies.

4. At the end of Phase II, a report was to be written presenting the experimental details of the laboratory tests, the results, and the conclusions.

D. TECHNICAL APPROACH

Laboratory facilities were established as required. These included a laboratory-scale apparatus for testing extinguishment and emissions. This Laboratory Extinguishment and Emissions Test Chamber (LEETC) uses Fourier transform infrared (FTIR) spectroscopy for characterization of emissions during extinguishment.

Sufficient testing was performed to allow characterization of the LEETC for Class B fires. In addition, cup-burner testing was performed to extend and improve those values reported under the Halon 1211 Phase II task (Reference 11).

Additional work on the fire-extinguishment algorithm has been performed; however, for convenience, this work has been documented under the Phase I effort (Reference 10). Moreover, an extensive overview of QSAR work is contained in the report on the Phase II effort for Halon 1211 in order to keep related data together (Reference 11).

E. DEFINITIONS

The report for the Phase I effort for Halon 1301 replacement presents a thorough overview of environmental considerations, nomenclature, fire chemistry, and other technology required to complete this task (Reference 10). At this time, however, some basics must be reviewed to permit an understanding of the work described in the present report.

A halon "substitute" is any agent, equipment, or engineering procedure that can be substituted for the use of halon, all or in part. Halon substitutes can be divided into two types. Halon "replacements" are halon-like halocarbon agents. Halon "alternatives" are everything else. Alternatives include "alternative agents," such as dry chemical, foam, water, and carbon dioxide, and "alternative approaches," such as rapid response and no-protection options. This program concerns only halon replacements.

Halon replacements can be divided into two categories. First-generation replacements belong to chemical classes that have been relatively well investigated, although a complete set of physical, chemical, and toxicological data may not exist for each individual compound. The list of such agents is primarily composed of the hydrochlorocarbons (HCFCs), the hydrofluorocarbons (HFCs), and the perfluorocarbons (FCs or PFCs). Second-generation replacements have chemical features (primarily the presence of bromine and/or iodine) that give fire extinguishment efficiencies equal to or better than those of the present halons, but also have molecular designs that provide a low tropospheric lifetime. Since few of the required properties are known for the second-generation replacements and many of these chemicals are not available in quantities that allow testing, the Air Force has decided to emphasize first-generation replacements in this project.

SECTION II

ESTABLISHMENT OF LABORATORY FACILITIES

A. NMERI CUP BURNER

As part of previously reported work, three different cup burners for laboratory-scale agent evaluation (full-scale, 5/8-scale, and 2/5-scale) were developed. The cup-burner design, procedures for use, and calibration are discussed in detail in Reference 7. The work cited shows that the 5/8-scale cup burner gives the most consistently reproducible results while minimizing the quantity of agent required for reliable testing. This cup burner is the one usually employed in halon replacement work at New Mexico Engineering Research Institute (NMERI).

B. LEETC APPARATUS

Preliminary results from total discharge testing at the Naval Research Laboratory (NRL) show that for discharge and extinguishment times of 10 seconds or less, Halon 1301, Halon 1211, and HBFC-22B1 give hydrogen fluoride concentrations in the hundreds of ppm by volume range; whereas, FC-3-1-10, HFC-227ea, HFC-125, and HFC-23 gave hydrogen fluoride concentrations from several thousand ppm to as high as 1 percent for some agents¹. Other researchers have also reported high concentrations of toxic products. For this reason, construction of a test chamber to allow testing of both extinguishment and emissions was required.

The NMERI LEETC is a 175-liter enclosed metal test chamber, which can be placed in a standard-sized fume hood (Figure 1). The apparatus is used to

¹ Baldwin, S. P., Brown, R., Burchell, H., Eaton, H. G., Salmon, G., St. Aubin, J., Sheinson, R. S., and Smith, W. D., "Halon Replacements: Cup Burner and Intermediate Size Fire Evaluation," International CFC and Halon Alternatives Conference, 29 September - 1 October 1992, Washington, DC.

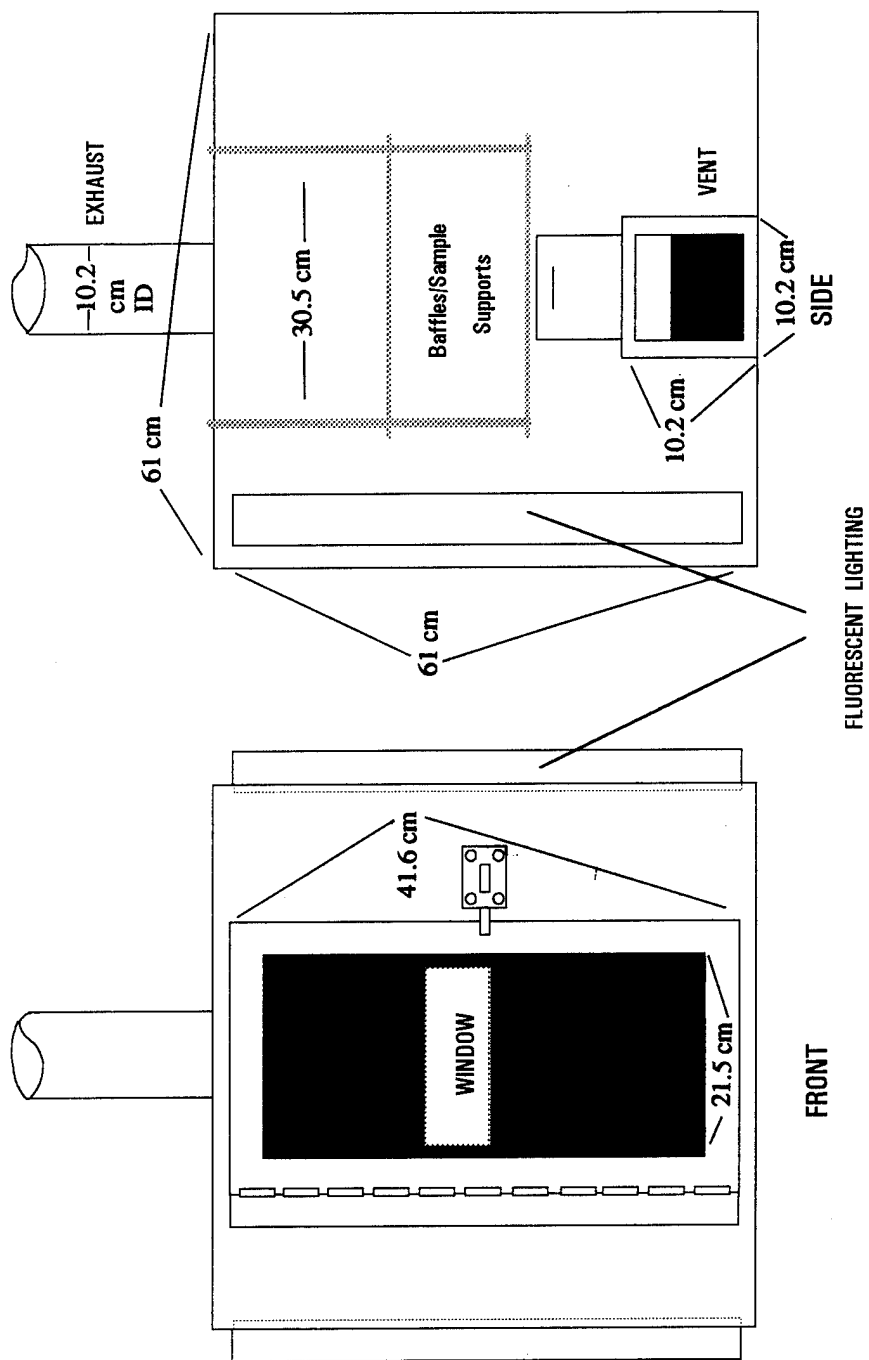


Figure 1. NMERI Laboratory Extinguishment and Emissions Test Chamber.

(1) determine extinguishment characteristics of total-flood agents and (2) characterize and quantify emission products from extinguished fires.

The walls and bottom of the chamber (LEETC) are 3/16-inch nickel-plated aluminum mounted on a steel frame. To avoid possible warping with large fires, the top is constructed of 3/16-inch nickel-plated steel. Nickel plating is used to reduce the interaction of the emission products and chamber materials. A hinged door at the front provides access, and a 8 1/4- by 16-inch window allows a viewing area of 132 in.² for visual observation and video documentation. Two 4- by 4-inch vents, which can be opened to varying degrees, are placed on the centerline toward the bottom of each side. The opening in the 4-inch ID chimney on the center of the top plate can be adjusted with a damper. This chimney can also be blocked by a plate laid across the top. Fluorescent lights running from top to bottom toward the front of each side panel provide interior lighting. Two 12- by 12-inch baffle plates centered within the chamber are suspended by four threaded posts and can be adjusted to varying heights. These baffles are normally horizontal. Table 1 gives the internal dimensions of the LEETC.

A port at the side of the LEETC allows continuous withdrawal of gaseous products into a 10-centimeter pathlength cell with potassium bromide (KBr) windows for FTIR spectroscopic analysis. Alternatively, an in situ sampling arrangement with a 17.5-centimeter pathlength can be installed with a periscope arrangement through the two air inlet doors. The FTIR spectrometer is a Perkin-Elmer System 2000 equipped for high-resolution (0.2 cm^{-1}), and time-resolved infrared (TRIR) absorption spectroscopy. The spectrometer can also perform IR (infrared) emission spectroscopy. The FTIR spectrometer is connected to a 486-computer operating under MS-DOS (Microsoft Disk Operating System) and equipped with two data acquisition boards including five co-processors with 30-MFLOPS calculation speed.

TABLE 1. NMERI LEETC INTERNAL DIMENSIONS AND VOLUMES.

Component	Height (cm)	Width (cm)	Depth (cm)	Volume (liters)
<u>Uncorrected</u>				
	56.59	56.36	56.69	180.83
<u>Corrections, Additions to Volume</u>				
Right Air Inlet Door	10.31	10.16	0.46	0.05
Left Air Inlet Door	10.16	10.16	0.46	0.05
Access Door	45.67	30.91	0.46	0.65
Window Cutout	41.66	21.59	0.46	0.41
<u>Corrections, Subtractions for Occupied Volume</u>				
Angle Iron	0.50	2.00	678.59	1.36
Top Deflection Plate	0.28	30.7	30.3	0.26
Bottom Deflection Plate	0.28	30.6	30.8	0.26
Threaded Posts	^a 0.90	142.24	0.09	
Nuts and Washers				0.04
Lights				4.56
NET VOLUME OF CHAMBER				175.43

^aDiameter.

SECTION III

LABORATORY CUP-BURNER TESTING

A. TEST PROCEDURES

Cup-burner testing was performed using the procedures described elsewhere (Reference 7). Different test methods are used depending on the boiling point of the material to be tested. Agents that are gases at room temperature are tested by removing the gas directly from a cylinder and running it through the appropriate flow meters. Extinguishment concentrations of agents that have relatively high boiling points are metered with a syringe pump into a heated vaporization compartment just below the cup burner. Agents that have boiling points near room temperature (approximately 25 ± 10 °C) are extremely difficult to measure, since such materials do not vaporize well from cylinders, but have a sufficiently high vapor pressure that a syringe pump is difficult to use. A novel method using a capped buret was developed to obtain cup-burner extinguishment concentrations for such materials; however, results obtained by this method can best be described as tentative. Future work is required to find suitable modifications of this method that will allow reliable extinguishment concentrations to be obtained for agents with intermediate boiling points.

Extensive studies of the experimental variables that may affect the accuracy and precision of cup-burner results were performed to validate the extinguishment concentrations obtained by these procedures. Some of these studies have been reported previously (Reference 7). During this program, this work was expanded with studies of flow measurement errors and the sensitivities of extinguishment concentrations to these errors. Analyses of measurement and calculation techniques indicate that the inherent errors in the measurement of air and agent flow are most critical in determining the precision of the extinguishment concentration. An extensive series of measurements was made to determine the magnitude of these errors. Results of these measurements are presented in Table 2.

TABLE 2. EVALUATION OF MEASUREMENT ERROR IN CUP-BURNER EXPERIMENTS.

Measurement	Number of Samples	Mean Value (mL/min)	95% (2 σ) Conf. Limit (mL/min)
Air Flow	43	7322	± 655 (8.9%)
Gaseous Agent Flow High Rate	12	1494	± 35 (2.3%)
Gaseous Agent Flow Intermediate Rate	12	1001	± 14 (1.4%)
Gaseous Agent Flow Low Rate	12	496	± 11 (2.2%)
Liquid Agent Flow High Rate	10	3.73	± 0.22 (5.9%)
Liquid Agent Flow Low Rate	10	2.44	± 0.18 (7.4%)

These inherent measurement errors result from the difficulties in reading gas burets or syringes and measuring time with stopwatches. When these errors are propagated through the extinguishment concentration calculation, they result in 95 percent confidence limits of 10.1 percent (gases) and 17.9 percent (liquids) of the extinguishment concentration reported. These values correspond to standard deviations of 5.0 percent and 8.8 percent of the mean value, respectively.

A survey of the literature and halon industry contacts indicates that at least five other organizations utilize cup burners to measure fire-extinguishing capabilities. Table 3 provides a comparison of extinguishment results from these other laboratories.

TABLE 3. INTERLABORATORY COMPARISON OF CUP-BURNER EXTINGUISHMENT CONCENTRATIONS.

Agent	NMERI ^a	NRL ^b Res. Lab.	GLCC ^c Lakes	ICI ^d	Univ. ^e of Tenn.	Fenwal ^f	Mean	Std. ^g Dev. Percent
HFC-23	12.4	12.0	12.7	-	12.6	12.0	12.3	2.2
HFC-125	9.4	8.8	9.3	-	-	8.1	8.9	5.2
FC-3-1-10	5.5	5.2	4.1	-	5.7	5.5	5.2	10.1
FC-5-1-14	4.4	-	-	-	-	4.4	4.4	0
H-1211	3.2	3.6	3.3	3.8	3.5	3.8	3.5	6.5
H-1301	2.9	3.1	3.1	3.6	2.7	3.0	3.1	9.0
HFC-227ea	6.3	6.6	6	-	-	5.8	6.2	4.4
HBFC-22B1	4.4	4.1	3.9	4.6	-	3.9	4.2	6.1
N ₂	31	30	-	30	-	-	30.3	1.3
CO ₂	20.4	21	-	21	-	28	22.6	12.4

^a Reference 7

^b Sheinson, R. S., personal communication, August 1992.

^c Reference 12

^d Fletcher, N., Wild, J. D., and Winterton, N., "Clean Agent Fire Extinguishants: A Low Ozone Depleting Potential Transitional Substitute," *1991 International Conference on CFC and Halon Alternatives*, Baltimore, MD.

^e Reference 13

^f Senecal, J. A., *Halon Replacement Chemicals: Perspectives on the Alternatives*, International Telecommunications Fire Protection Symposium, New Orleans, LA, 1992.

^g Standard Deviation as a percentage of the mean value. Note that single outlier values for FC 3-1-10, H-1301, and CO₂ account for large deviations for these compounds.

Analysis of the available data indicates that, despite the differences in cup-burner design and variations in test techniques, the extinguishment values for compounds agree well between laboratories, generally within 10 percent, which is approximately the same variability as is predicted based on error analysis (Figures 2 and 3).

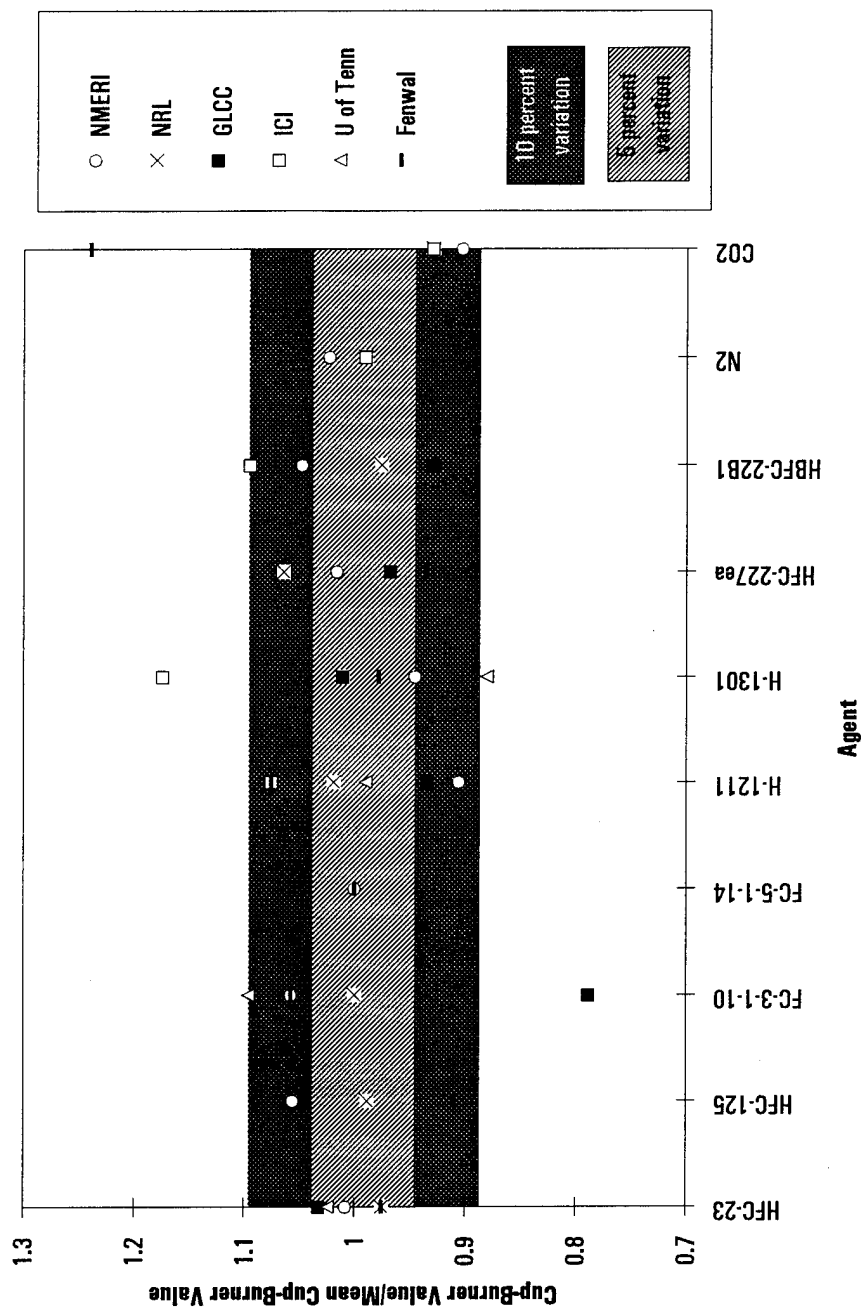


Figure 2. Comparison of Cup-Burner Extinguishment Concentrations by Various Laboratories.

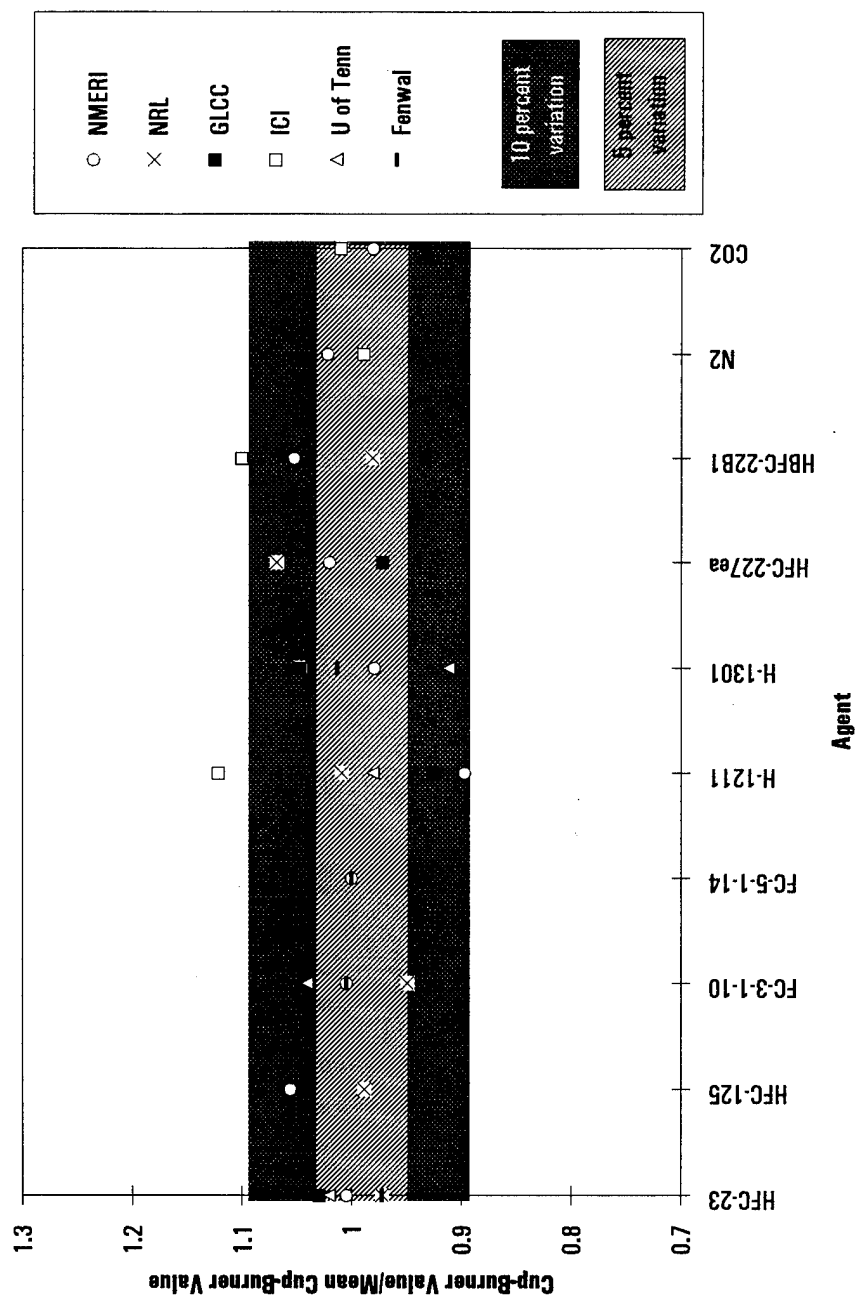


Figure 3. Comparison of Cup-Burner Extinguishment Concentrations--Outliers Removed.

B. EXTINGUISHMENT TEST RESULTS

All of the cup-burner work reported herein employed *n*-heptane as the fuel. Average extinguishment concentrations for the materials tested are presented in Tables 4 and 5. The values presented in these tables have been rigidly scrutinized for possible experimental errors, suitability for testing with available methods, flammability, and other factors that might affect the reported values. The values reported in Table 4 have met all the criteria required for full confidence in their values subject to the limitations presented above. The values presented on Table 5 are, for various reasons (e.g., flammability, limited quantities, boiling point, questionable experimental conditions), believed to be of limited reliability and are presented for completeness only.

C. CONCLUSIONS

The test results further confirm that (1) bromine- and iodine-containing compounds have extinguishment capabilities much better than other materials and (2) no first-generation agent (HCFC, HFC, or FC) is likely to have an extinguishment capability similar to that of the present halons.

Concern has been expressed about the lack of standardization for cup burners and procedures.² The testing performed under the Air Force programs has shown that the 5/8-scale burner provides reasonably precise results that compare well with published results of other researchers. Given the acknowledged advantage of this apparatus in terms of sample size, it is recommended that it be used as a standardized cup burner through development of an ASTM (American Society for Testing and Materials) or NFPA (National Fire Protection Association) standard.

² Comments at the meeting of the National Fire Protection Association (NFPA) Technical Committee on Alternative Protection Options to the Halons, Kennedy Space Center, FL, 8-10 March 1993.

TABLE 4. FULL CONFIDENCE CUP-BURNER EXTINGUISHMENT
CONCENTRATIONS.^a

Halocarbon No.	Halon No.	IUPAC Name	CAS No.	Concentration (%)
10	104	Tetrachloromethane (carbon tetrachloride)	56-23-5	7.6
11	113	Trichlorofluoromethane	75-69-4	7.8
12	122	Difluorodichloromethane	75-71-8	7.6
12B1	1211	Bromochlorodifluoromethane	353-59-3	3.2
13	131	Chlorotrifluoromethane	75-72-9	7.3
13B1	1301	Bromotrifluoromethane	75-63-8	2.9
13I1	13001	Trifluoroiodomethane	2314-97-8	3.0
14	14	Tetrafluoromethane	75-73-0	13.8
20	103	Trichloromethane	67-66-3	10.5
21B2	1202	Dibromodifluoromethane	1858-53-7	1.8
22	121	Chlorodifluoromethane	75-45-6	11.6
22B1	1201	Bromodifluoromethane	1511-62-2	4.4
23	13	Trifluoromethane	75-46-7	12.6
30	102	Dichloromethane	75-09-2	14.1
32	12	Difluoromethane	75-10-5	8.8
113	233	1,2,2-Trichloro-1,1,2-trifluoroethane	76-13-1	6.2
114	242	1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	6.4
114B2	2402	1,2-Dibromo-1,1,2,2-tetrafluoroethane	124-73-2	2.1
115	251	1-Chloro-1,1,2,2,2-pentafluoroethane	76-15-3	6.3
115I1	25001	Pentafluoroiodoethane	354-64-3	2.1
116	26	Hexafluoroethane	76-16-4	7.8

^a*n*-Heptane fuel, NMERI 5/8-scale cup burner.

^bNot applicable.

TABLE 4. FULL CONFIDENCE CUP-BURNER EXTINGUISHMENT
CONCENTRATIONS (CONTINUED).^a

Halocarbon No.	Halon No.	IUPAC Name	CAS No.	Concentration (%)
122	223	1,1-Difluoro-1,2,2-trichloroethane	354-21-2	6.3
123B2	2302	2,2-Dibromo-1,1,1-trifluoroethane	354-30-3	1.9
123aB2	2302	1,2-Dibromo-1,1,2-trifluoroethane	354-04-1	2.0
123aB1 α	2311	1-Bromo-2-chloro-1,1,2-trifluoroethane	354-06-3	3.2
124	241	2-Chloro-1,1,1,2-tetrafluoroethane	2837-89-0	8.2
124B1	2401	2-Bromo-1,1,1,2-tetrafluoroethane	124-72-1	2.9
125	25	Pentafluoroethane	354-33-6	9.4
132b	222	1,2-Dichloro-1,1-difluoroethane	1649-08-7	7.9
133a	231	2-Chloro-1,1,1-trifluoroethane	75-88-7	7.6
134	24	1,1,2,2-Tetrafluoroethane	359-35-3	11.2
134a	24	1,1,1,2-Tetrafluoroethane	811-97-2	10.5
142B1	2201	2-Bromo-1,1-difluoroethane	359-07-9	4.2
217baI1	37001	1,1,1,2,3,3,3-heptafluoro-2-iodopropane	677-69-0	3.22
17caI1	37001	1,1,2,2,3,3,3-heptafluoro-1-iodopropane	754-34-7	3.0
218ca	38	Octafluoropropane	76-19-7	6.1
225ca/cb	352	3,3-Dichloro-1,1,1,2,2-pentafluoropropane/1,3-Dichloro-1,1,2,2,3-pentafluoropropane (azeotrope)	127564-92-5	6.5
227ea	37	1,1,1,2,3,3,3-Heptafluoropropane	431-89-0	6.3
227cb	37	1,1,1,2,2,3,3-Heptafluoropropane	2252-84-8	6.5
236ea	36	1,1,1,2,3,3-Hexafluoropropane	431-63-0	6.6
236fa	36	1,1,1,3,3,3-Hexafluoropropane	690-39-1	5.6

^a*n*-Heptane fuel, NMERI 5/8-scale cup burner.

^bNot applicable.

TABLE 4. FULL CONFIDENCE CUP-BURNER EXTINGUISHMENT
CONCENTRATIONS (CONCLUDED).^a

Halocarbon No.	Halon No.	IUPAC Name	CAS No.	Concentration (%)
245cb	35	1,1,1,2,2-Pentafluoropropane	1814-88-6	8.2
C-318	48	Octafluorocyclobutane	115-25-3	7.2
319I1	49001	Nonafluoro-1-iodobutane	423-39-2	2.8
3-1-10	4-10	Decafluorobutane (perfluorobutane)	355-25-9	5.0
1343B1	b	4-Bromo-3-chloro-3,4,4-trifluoro-1-butene	374-25-4	4.5
1344B1	b	4-Bromo-3,3,4,4-tetrafluoro-1-butene	18599-22-9	3.5
C-5-1-12	b	Perfluoromethylcyclopentane	180-22-7	3.7
5-1-13I1	6-13-0-01	Tridecafluoro-1-iodohexane	355-43-1	2.5
5-1-14	6-14	Tetradecafluorohexane (perfluorohexane)	355-42-0	4.4
6-1-16	7-16	Hexadecafluoroheptane (perfluoroheptane)	355-57-9	4.0
b	b	Perfluoromethylcyclohexane	355-02-2	3.5
b	b	Perfluoro-1,3-dimethylcyclohexane	335-27-3	3.2
7-1-17B1	8-17-0-1	1-Bromo-heptadecafluorooctane	423-55-2	2.4
b	b	Perfluorodecalin	306-94-5	3.6
b	b	Chloropentafluorobenzene	344-07-0	5.4
b	b	1,3-Dichlorotetrafluorobenzene	1198-61-4	6.1

^a*n*-Heptane fuel, NMERI 5/8-scale cup burner.

^bNot applicable.

TABLE 5. AVERAGE CUP-BURNER EXTINGUISHMENT
CONCENTRATIONS OF LIMITED CONFIDENCE.^a

Halocarbon No.	Halon No.	IUPAC Name	CAS No.	Concentration (%)
31	111	Chlorofluoromethane	593-70-4	^b 20.0
121	214	1-Fluoro-1,1,2,2-tetrachloroethane	354-14-3	^c 7.8
123	232	2,2-Dichloro-1,1,1-trifluoroethane	306-83-2	^d 7.1
123a	232	1,2-Dichloro-1,1,2-trifluoroethane	354-23-4	^d 8.3
130a	204	1,1,1,2-Tetrachloroethane	630-20-6	^b 8.0
141b	212	1,1-Dichloro-1-fluoroethane	1717-00-6	^d 12.5
^e	^e	1-Bromo-3,3,3-trifluoro-1-propene	^e	^c 8.5
216ba	362	1,2-Dichloro-1,1,2,3,3,3-hexafluoropropane	661-97-2	^f 4.9
254cb	34	1,1,2,2 Tetrafluoropropane	40723-63-5	^f 10.1
270fa	302	1,3-Dichloropropane	142-28-9	^f 5.5
270da	302	1,2-Dichloropropane	78-87-5	^f 4.6
272ea	32	1,2-Difluoropropane	62126-90-3	^f 5.6
4-1-12	5-12	Dodecafluoropentane	678-26-2	^d 12.0

^a*n*-Heptane fuel, NMERI 5/8-scale cup burner.

^bQuestionable experimental conditions.

^cInsufficient quantity for accurate testing.

^dNear room temperature boiling point.

^eNot available.

^fFlammable compound.

SECTION IV

LEETC TESTING

A. TEST PROCEDURES

Procedures for Class B (liquid hydrocarbon fuels) fires have been developed, and initial work toward a Class A (cellulosic materials) procedure has been completed. The liquid fuel fires use small pans filled with *n*-heptane fuel. A list of pan sizes is shown in Table 6. This table also gives the ratio of the pan area to the LEETC volume expressed in units of square feet per 1000 cubic feet. This ratio has been widely used in scaling test fires; however, no theoretical background exists to support its use. It is usually accepted that ratios of around 0.06 represent small fires (relative to the test chamber volume); those around 0.6 correspond to medium-size fires, and those around 6 correspond to large fires.

As described above, the LEETC is equipped for both visual analysis of extinguishment events and FTIR analysis of agent concentrations and decomposition products. During the course of this program a series of experiments was conducted to demonstrate the application of these methods and to develop optimum procedures.

1. Class B Fires

a. Fourier Transform Infrared Spectroscopy (FTIR)

A detailed explanation of the theory and practice of infrared spectroscopy is beyond the scope of this work and is readily available in the literature (References 14 and 15). However, an understanding of a few basic principles is required for this study.

TABLE 6. FIRE PAN SIZES FOR LEETC CLASS B TESTING.

Fire Pan (Nominal)	Diameter (Measured) (cm)	Area (ft ²)	Area/Volume Ratio (ft ² /1000 ft ³)
1/4-inch nozzle	0.64	0.00035	0.056
1/2-inch pipe plug	1.28	0.00139	0.224
1/2-inch copper cap	1.63	0.00225	0.363
3/8-inch pipe cap	1.61	0.00219	0.355
3/4-inch pipe plug	1.79	0.00271	0.438
3/4-inch copper cap	2.26	0.00432	0.699
3/4-inch pipe cap	2.43	0.00499	0.808
Fabricated pan 1.5 in.	4.50	0.01712	2.770
Fabricated pan 3 in.	7.50	0.04756	7.695
Fabricated pan 4 in.	10.50	0.09321	15.083
Fabricated pan 8 in.	21.00	0.37286	60.333

Three distinct experimental modes are available for the study of extinguishment events with FTIR analysis: external absorption, in situ, and emission spectroscopy. Each experimental mode has specific advantages and disadvantages and produces complementary information. A block diagram of each experimental mode is presented in Figure 4.

In both the external and in situ modes, the modulated infrared beam from the spectrometer passes through the sample gas mixture to a detector. In these experiments, the detector is a wide-band MCT (mercury, cadmium, tellurium) detector cooled with liquid nitrogen to -196 °C. As the beam passes through the sample, the component gases absorb energy at characteristic wavelengths determined by the detailed molecular structure of the gas. By convention, the wavelengths in the range

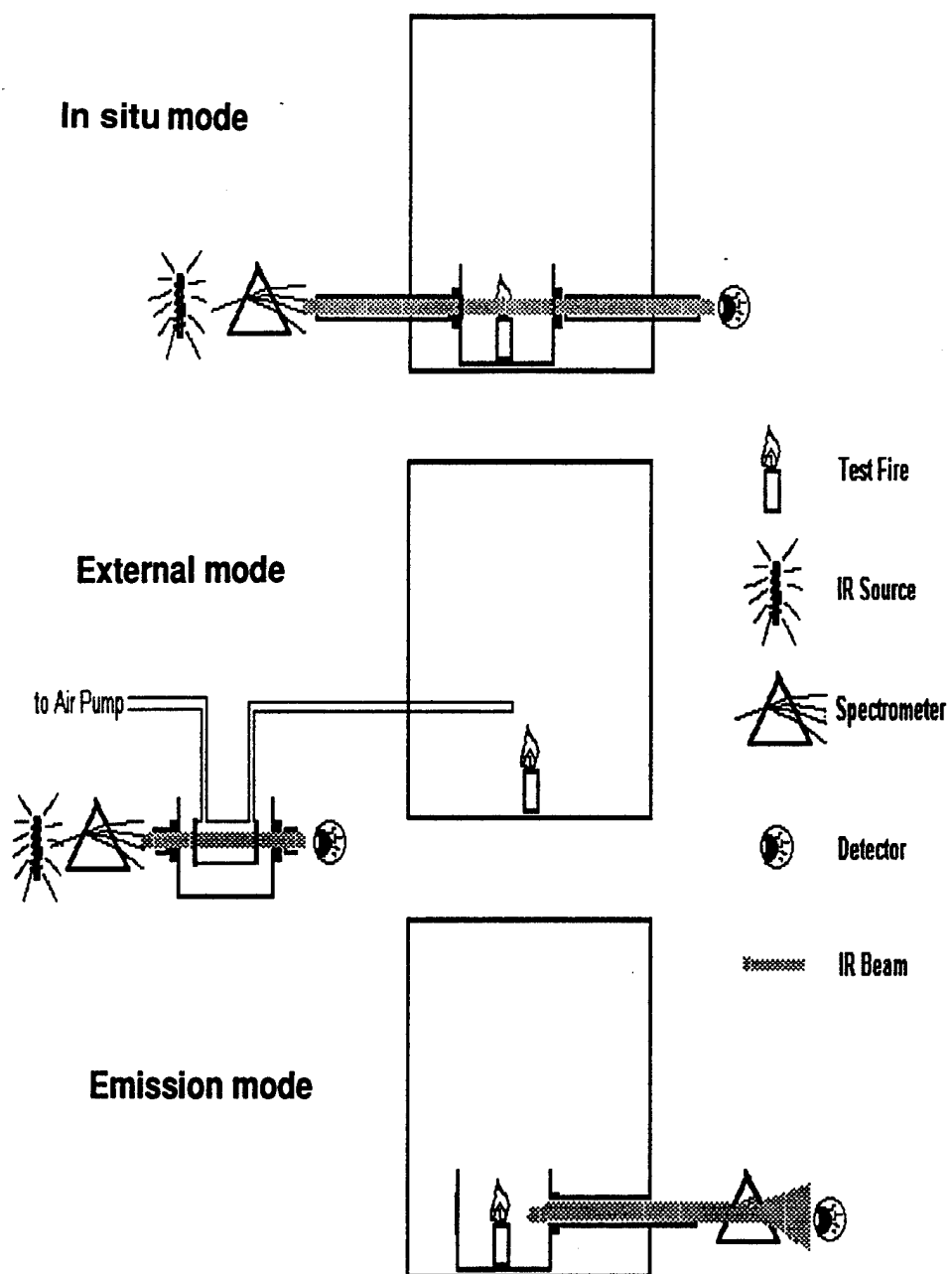


Figure 4. Block Diagram of Available FTIR Modes.

of 2 to 25 microns are converted to the corresponding energy in units of cm^{-1} .³ Table 7 contains the characteristic absorption energies of a number of compounds of interest.

In the emission mode, hot gases in the sample emit infrared radiation as they relax, once again at the same characteristic energies that are dependent on molecular structure. At high temperatures, such as those occurring in a flame, several temperature-dependent features become significant. First, additional absorption or emission peaks associated with excited molecular states add additional complexity to the spectrum. Second, the relative intensities of fine structure bands are distorted. Finally, many bands are considerably broadened. Detailed explanations of these effects are contained in Reference 14. Current efforts to use these effects to measure flame temperatures are described in References 16 and 17. The limited scope of this work precluded the use of these features for temperature measurement.

The spectra characteristic of the three different experimental modes are illustrated in Figure 5.

Spectrum A, recorded in the external absorption mode, is conventional in all respects. The intensities, band positions, and peak widths are in agreement with literature values. Because of the controlled sample conditions available in this mode, the concentrations of each of the constituent gases can be calculated with good precision. In an associated study (Reference 18), using a near-room-scale

³Infrared absorption spectra are routinely presented in two different styles — transmission and absorption. The transmission style is a "Peaks Down" style with the abscissa in units of percent transmission. The absorption style is a "Peaks Up" style with the abscissa in units of absorbance. There is an inverse logarithmic relationship between percent transmission and absorbance. By convention, reference spectra are presented in the transmission style. However, spectra used for obtaining concentrations of absorbing compounds are always presented in the absorbance style as the absorbance is linear with respect to concentration. Emission spectra are always presented in a "Peaks Up" style in units of intensity. The spectra in this report are presented in the style appropriate to the most accurate communication of the data.

TABLE 7. INFRARED BANDS OF SELECTED COMPOUNDS.

Compound	Band location (cm ⁻¹)	Comments
HF	4250 to 3700	Multiple, regular, sharp bands separated by 37.3 cm ⁻¹
H ₂ O	3850 to 3400; and 1850 to 1400	Multiple, sharp bands with irregular spacing
Hydrocarbons (in general)	3100 to 2800	Multiple, sharp bands in simple compounds; multiple broad bands in complex compounds
CO ₂	2400 to 2300; 661	Overlapping strong bands, peak at 661 cm ⁻¹ extremely sharp spike
CO	2200 to 2100	Multiple, regular, sharp bands separated by 3.6 cm ⁻¹
COF ₂	1980 to 1900	Distinctive structure, two broad lobes with a weak sharp spike between them
Fluorocarbons (in general)	1500 to 800	Very strong, multiple bands, typically off-scale even at low concentrations

(645-ft³) chamber, this method is used to obtain extensive data on the concentrations of toxic decomposition products in a large series of test extinguishments. The primary concern with this experimental mode is the possible interaction of combustion gases with the sampling system. A detailed analysis of this potential problem and its solution are contained in Reference 18.

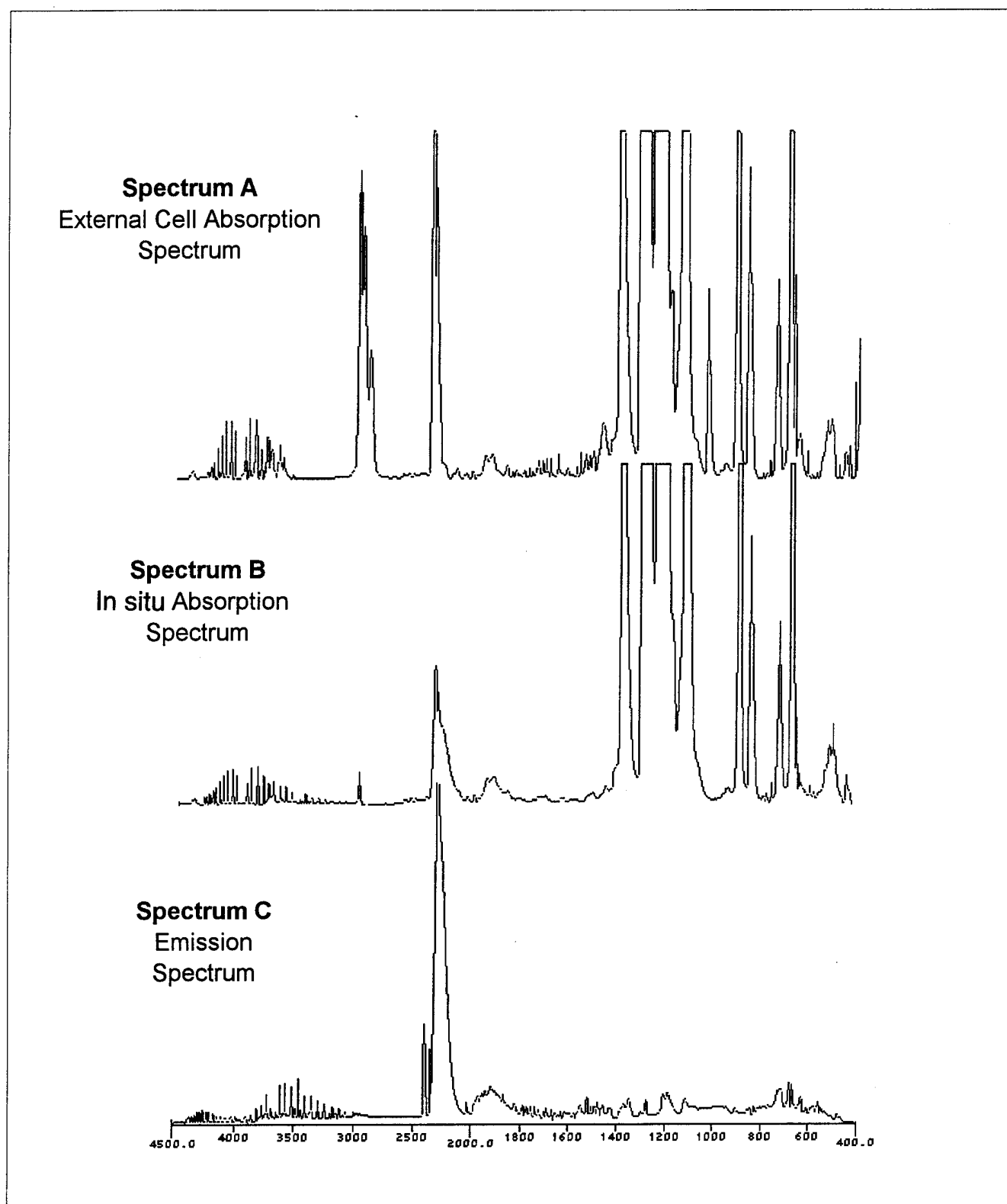


Figure 5. Comparison of FTIR Spectra in Three Modes Showing HFC-227ea Spectra.

Spectrum B, recorded in the in situ absorption mode, shows some of the advantages and disadvantages of this mode when compared with the external mode (Spectrum A). Note particularly the increased complexity of the hydrogen fluoride region from 4300 to 3600 cm^{-1} . This complexity results from the "hot" bands of excited hydrogen fluoride produced by the interaction of the extinguishing agent and the flame.

Also of interest is the broadening of the carbon dioxide band at about 2360 cm^{-1} . These spectral features, only observable in the in situ mode, provide significant information about the detailed interaction of the agent and flame. The use of this information is discussed in the following section on time-resolved infrared spectroscopy (TRIR). These "hot" spectral features complicate the determination of quantitative concentrations and are quite dependent on the movement of the flame in response to air currents.

Spectrum C was recorded in the emission mode. This mode clearly shows the effect of the excited molecules, the emissions of which are the primary features of the spectrum. Black body radiation creates an overall emission background. An interesting feature of this spectrum is the series of down peaks below 1500 cm^{-1} . These peaks result from the absorption of energy by the agent in the space between the flame and the IR window. The lack of agent emission peaks suggests that the agent is entirely consumed by the flame. A detailed spectroscopic study of flame-agent interactions was beyond the scope of this study, but such a study would yield valuable information, useful in designing a second-generation agents program, while minimizing decomposition products.

b. Time-Resolved Infrared Spectroscopy (TRIR)

A special feature of the NMERI FTIR spectrometer is its ability to collect spectral data at very high rates. At low resolution, 16 cm^{-1} , 20 spectra per minute can be collected in TRIR. This resolution is not adequate for detailed gas-phase spectroscopy, which is often performed at resolutions of 0.2 cm^{-1} , a rate far too

high to enable spectra collection in a time resolved mode. For the NMERI experiments, a compromise resolution of 2 cm^{-1} was chosen allowing a data acquisition rate of approximately 2.5 spectra per second. Figure 6 is a stack plot of spectra obtained at this data rate and temporally centered about the extinguishment event.

2. Class A Fires

Very preliminary work was performed with Class A fires. The paper fuel consisted of approximately 14 grams of fan-folded brown paper, 10 centimeters high by 18 centimeters wide. The paper fuel fires were prepared using 5 sheets of brown paper, single-ply towels, folded in half and pleated at 2.5-centimeter intervals. Paper samples ranged in weight from 14.0 to 14.3 grams and averaged 14.1 grams with a standard deviation of 0.1 grams. One end of the fan was placed in a 2.5-centimeter copper tube fitting. The other end was spread to obtain an 18-centimeter overall width. Repeated control tests showed consistent flame appearance and uniform flame size during the period of 20 to 70 seconds after ignition.

Although data for laboratory-scale Class A fires are reported here, this work represents one of the first efforts to develop a true laboratory-scale Class A fire test using cellulosic material. At present, no acceptable method for agent testing in the laboratory exists for Class A fuels. Development of a standard laboratory Class A fire will require an extensive set of experiments aimed at establishing comparability with the woodcrib fires used for large-scale testing.

B. EXTINGUISHMENT TEST RESULTS

Table 8 contains a limited set of extinguishment test data for HFC-227ea and Halon 1301 using a conventional approach of measuring extinguishment time by reviewing videos, and calculating concentrations from agent weight and chamber volume. Table 9 contains a data set obtained using TRIR measurements in the in situ mode. TRIR data analysis results for these experiments are included (Appendix A).

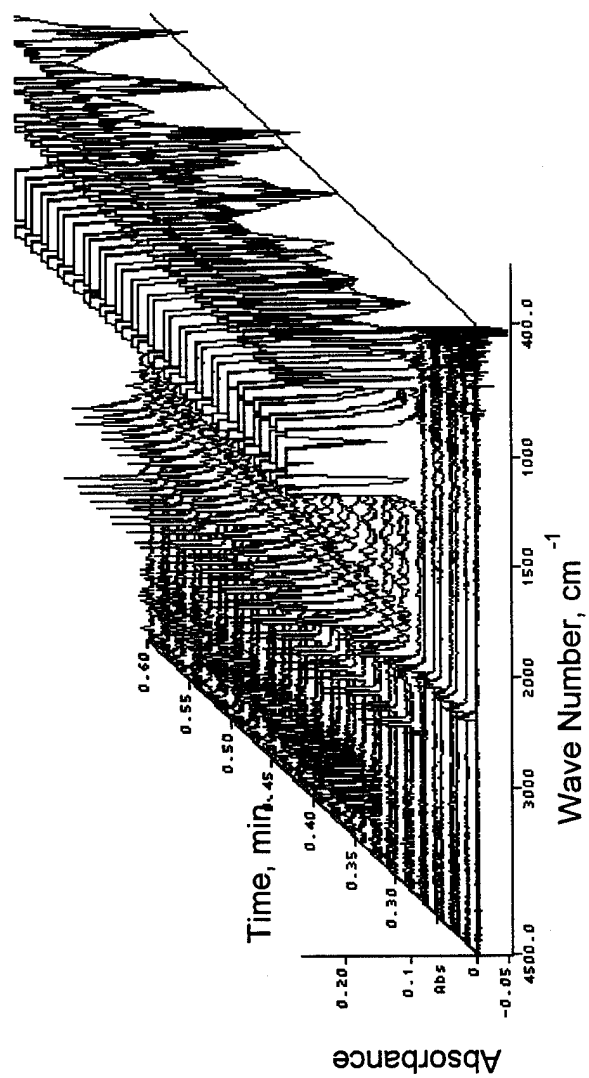


Figure 6. TRIR Stack Plot at 2.0 cm⁻¹ Resolution, ~ 2.5 Spectra per Second.

TABLE 8. SELECTED LEETC CLASS B EXTINGUISHMENT TEST RESULTS.

Pan Diameter (cm)	Agent Amount (grams)	Agent Concentration (%)	Extinguishment Time (sec)
<u>Halon 1301</u>			
1.6	15.0	1.7	No extinguishment
	20.0	2.22	<1
<u>HFC-227ea</u>			
1.6	25.1	2.45	No extinguishment
	30.0	2.90	No extinguishment
	34.9	3.35	No extinguishment
	49.9	4.75	122
	55.1	5.22	7
	59.9	5.64	8
	70.0	6.51	5
10.5	25.2	2.45	10.1
	30.2	2.91	8
	39.9	3.84	7
	50.5	4.80	7

TABLE 9. EXTINGUISHMENT CONCENTRATIONS FROM FTIR EXPERIMENTS.

Agent	Calculated Concentration (%)	Extinguishment Time (sec)	FTIR Concentration at Extinguishment (%)	FTIR Concentration after Extinguishment and Mixing (%)
Halon 1301	2.22	5.8	1.5	2.3
FC-227ea	4.75	3.1	4.5	5.6
C-3-1-10	5.18	5.0	4.4	5.1
FC-23	7.9	13.9	8.4	9.9

C. EMISSION TEST RESULTS

A large amount of test data has been collected on emissions to verify the utility of the LEETC and the associated FTIR spectrometer to monitor emissions over time. More than 200 megabytes of raw spectral data have been archived on magnetic tape. Analysis of these data was performed by examination of three-dimensional stack plots (Figure 7), individual spectra (Figure 8), and the detailed measurement of absorbance peak heights. Figures 9, 10, and 11 show expanded views of the stack plots indicating regions of particular interest. The TRIR data analysis results in Appendix A show many examples of these plots.

One example of the power of this approach is shown in Figure 12a, where an unusual series of transient strong peaks appears in the fluorocarbon region for a few seconds between the start of HFC 227ea discharge and extinguishment. The precise location and peak shapes were obtained by examination of the individual spectrum corresponding to time of maximum peak intensity (Figure 12b). A review of the

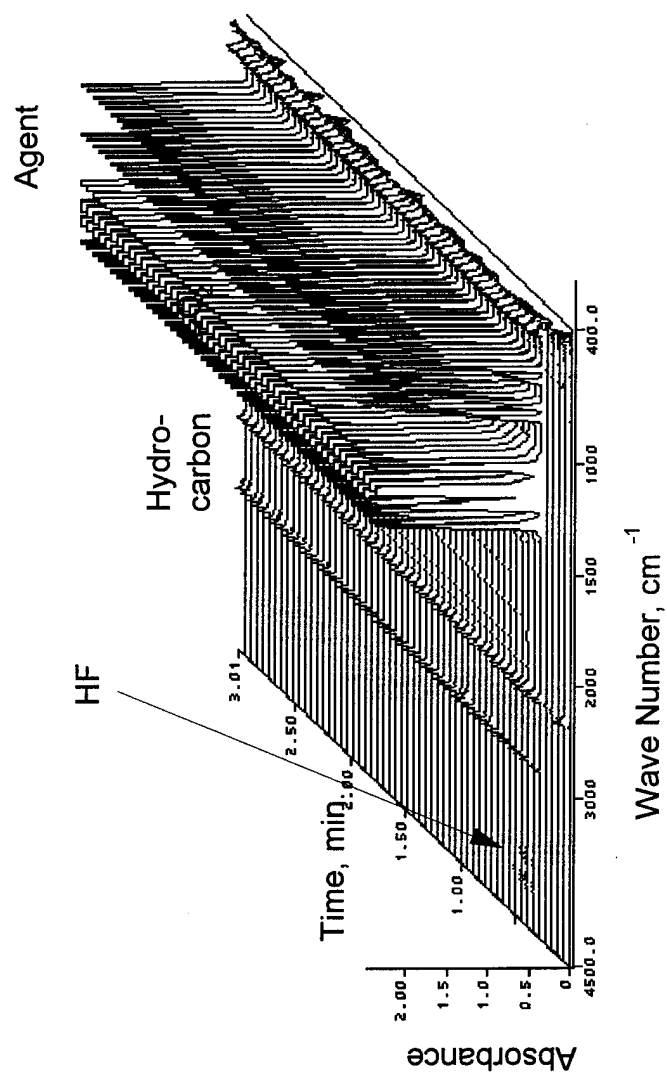


Figure 7. TRIR Stack Plot of an HFC-227ea Extinguishment, Showing the Complete Data Range.

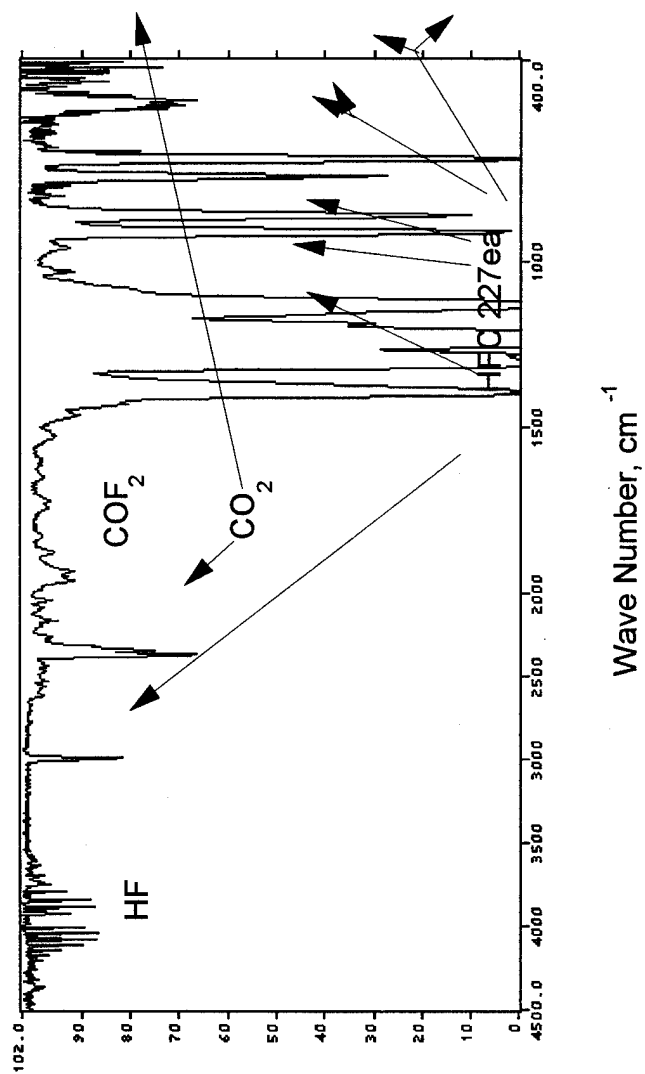


Figure 8. Typical Spectrum from an HFC-227ea Extinguishment in External Absorption Mode.

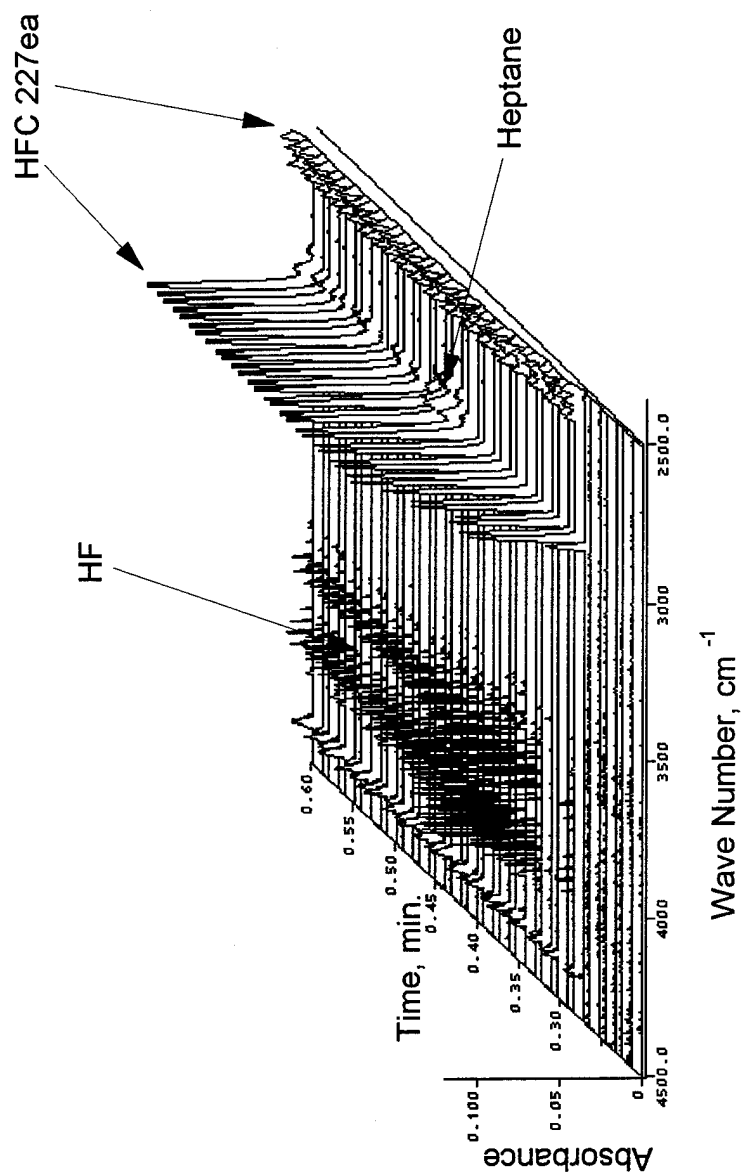


Figure 9. TRIR Stack Plot from an HFC-227ea Extinguishment in External Absorption Mode Featuring HF and Hydrocarbon Bands.

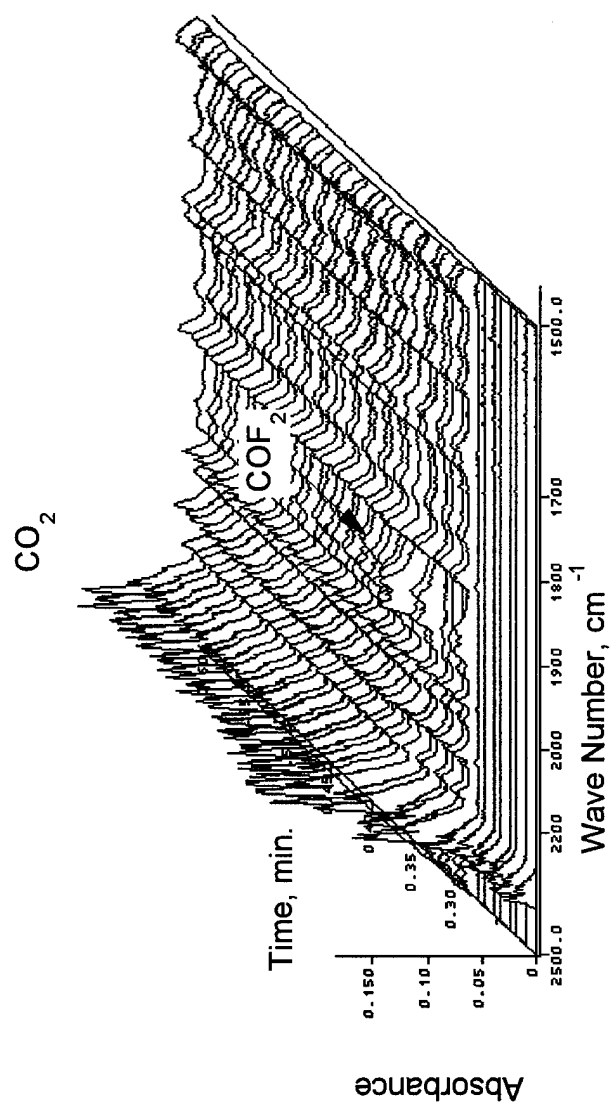


Figure 10. TRIR Stack Plot from an HFC-227ea Extinguishment in External Absorption Mode Featuring CO_2 and COF_2 Bands.

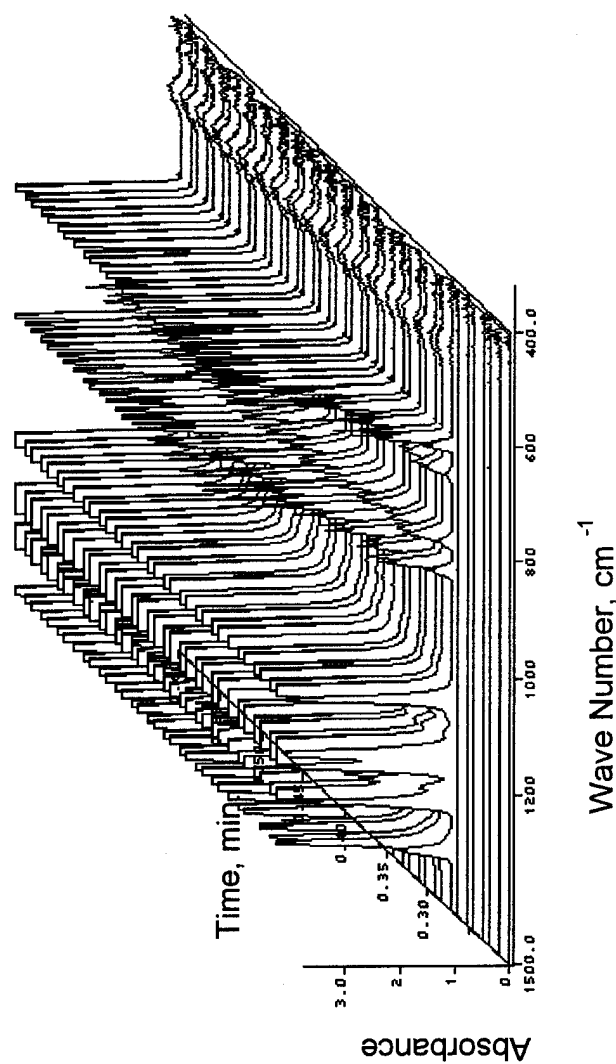
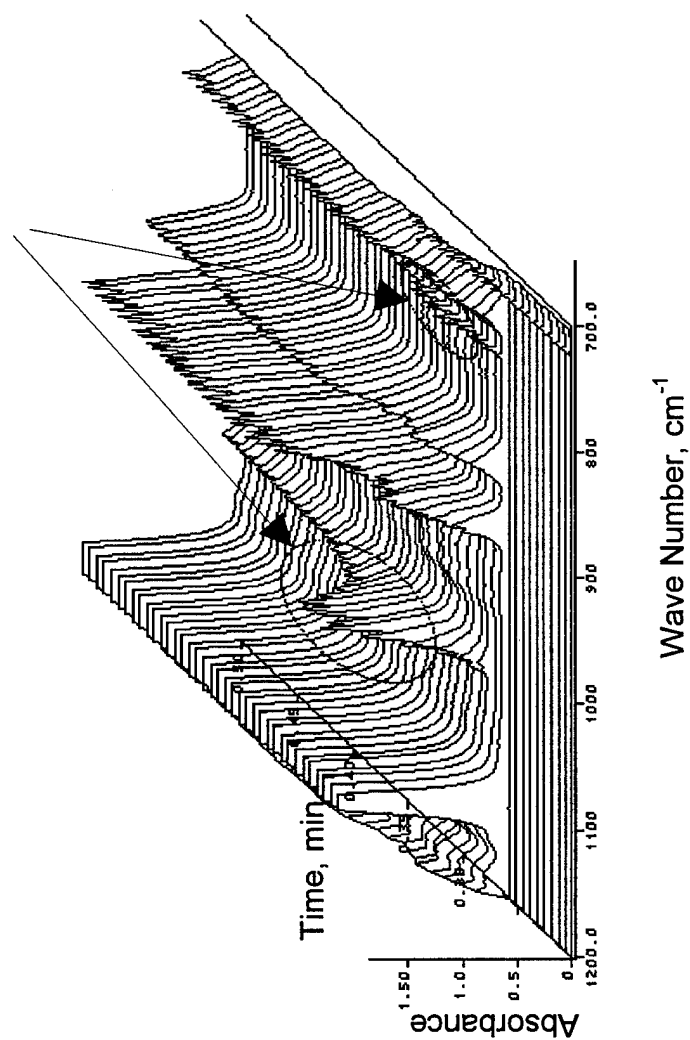


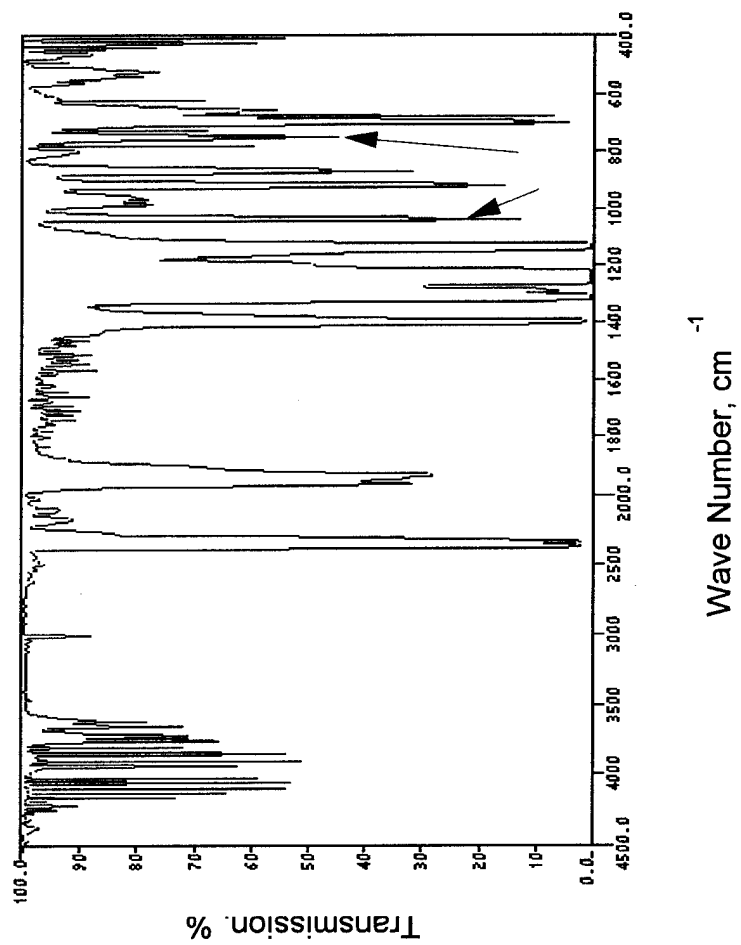
Figure 11. TRIR Stack Plot from an HFC-227ea Extinguishment in External Absorption Mode Showing Agent Peaks.

New Spectral Features



(a) TRIR Stack Plot Showing Peaks.

Figure 12. TRIR Stack Plot from an HFC-227ea Extinguishment in External Absorption Mode.



(b) External Absorption Spectrum 0.5 Minutes After Discharge.

Figure 12 TRIR Stack Plot from an HFC-227ea Extinguishment in External Absorption Mode (Concluded).

literature (Reference 19) revealed that these peaks are probably from perfluoropropene, which would be produced by the following reaction:



While this compound has not previously been reported as a decomposition product of HFC-227ea, it is the typical product of a dehydrohalogenation reaction and probably would be expected. This compound is reported in the standard industrial toxicology treatises and is believed to be "mildly toxic by inhalation." The reported LC₅₀ by inhalation, 4-hour exposure, is 1825 ppm for rats and 750 ppm for mice (Reference 20). The concentration of the sample in Figure 12b is about 2 percent based on comparisons with the reference spectrum. Detailed concentration analysis would require purchase of pure perfluoropropene and preparation of calibration samples.

Extensive studies of extinguishment concentrations and decomposition product formation have been performed in a 645-ft³ chamber and are probably more representative of real world situations. These results are reported in Reference 18. Comparison studies of Halon 1301 and three major replacement candidates are reported in Tables 9 and 10.

TABLE 10. COMPARISON OF DECOMPOSITION PRODUCTS.

Agent	Calculated Agent Concentration (%)	HF Concentration (ppm)		COF ₂ Concentration (ppm)	
		Maximum	After Mixing	Maximum	After Mixing
Halon 1301	2.2	92	a	a	a
HFC 23	7.9	290	7	9.5	1.7
HFC 227ea	4.75	311	2	6.1	a
FC-3-1-10	5.2	604	4	52.1	a

^aNot detectable.

SECTION V

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The LEETC provides valuable and detailed information on extinguishment and on agent decomposition products under total-flood conditions. The use of FTIR technology provides a powerful tool for identifying and quantifying decomposition products. The additional capabilities of TRIR spectroscopy provide key details of the extinguishment event and can be used to understand more fully both the mechanisms of extinguishment and the distribution of agents in a total flood environment.

The most likely first-generation replacement agents, HFC-227ea, HFC-23, and FC-3-1-10 all produce significantly higher quantities of the highly toxic decomposition products, hydrogen fluoride and carbonyl fluoride, than does Halon 1301.

No first-generation agent (hydrochlorofluorocarbon, hydrofluorocarbon, or perfluorocarbon) will provide extinguishment equivalent to that obtained with the present halons.

B. RECOMMENDATIONS

(1) Investigations of second-generation Halon 1301 replacement agents should be initiated.

(2) Work should be performed to develop cup-burner methodologies and or equipment that will permit facile determinations of extinguishment concentrations for agents with boiling points near room temperature.

(3) Work should be performed to develop a standard for the 5/8-scale cup burner to allow good interlaboratory agent comparisons.

(4) Additional work should be carried out to evaluate decomposition products as a function of agent type.

(5) The use of fire size expressed in square feet of pan surface per 1000 cubic feet of volume probably needs reevaluation. This ratio is widely used in testing total-flood agents; however, the use appears to be primarily historical.

(6) Work to develop a good laboratory-scale test for total-flood agents in Class A fires of cellulosic materials should be continued. At present, only expensive, large-scale, wood crib fire tests are used to determine Class A performance.

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APPENDIX A

REPRESENTATIVE TRIR DATA SETS

This appendix contains representative TRIR data for small, $0.69 \text{ ft}^2/1000 \text{ ft}^3$ fires using the in situ absorption mode.

TABLE A-1. TIME RESOLVED INFRARED (TRIR) SPECTROSCOPY.

Agent	Halon 1301	Weight	20.0 gm.	Concentration	2.25%
Fire	.69 Cu Cap	Nozzle	Sprayco 1/4N - 2	Pressure	600 lb/in. ²
Sampling	insitu	Pathlength	175mm	Resolution	2 cm ⁻¹

Notes

Quantitative Data

Time Absolute	Time Rel. Discharge	Concentrations				
		Agent, %	HF, ppm	CO ₂ , %	CO, ppm	COF ₂ , ppm
0.2381	-0.0129	0.00	0	0.33	122	0
0.2446	-0.0064	0.00	0	0.34	130	0
0.251	0	0.00	0	0.18	0	0
0.2639	0.0129	0.05	0	0.47	95	0
0.2703	0.0193	0.29	52	0.63	25	0
0.2767	0.0257	0.41	46	0.49	129	0
0.2831	0.0321	0.63	79	0.67	151	0
0.2896	0.0386	0.70	94	0.52	155	0
0.296	0.045	0.80	109	0.56	170	0
0.3025	0.0515	0.81	110	0.54	115	0
0.3089	0.0579	1.01	88	0.45	83	0
0.3153	0.0643	1.09	105	0.50	160	0
0.3218	0.0708	0.91	155	0.69	157	0
0.3282	0.0772	1.13	126	0.61	182	0
0.3347	0.0837	1.35	124	0.43	123	0
0.3474	0.0964	1.52	84	0.30	25	0
0.3989	0.1479	1.60	31	0.22	0	0
0.4954	0.2444	2.04	0	0.20	0	0
0.5983	0.3473	2.33	0	0.22	0	0
0.9969	0.7459	2.52	0	0.22	0	0
1.1962	0.9452	2.52	0	0.20	0	0

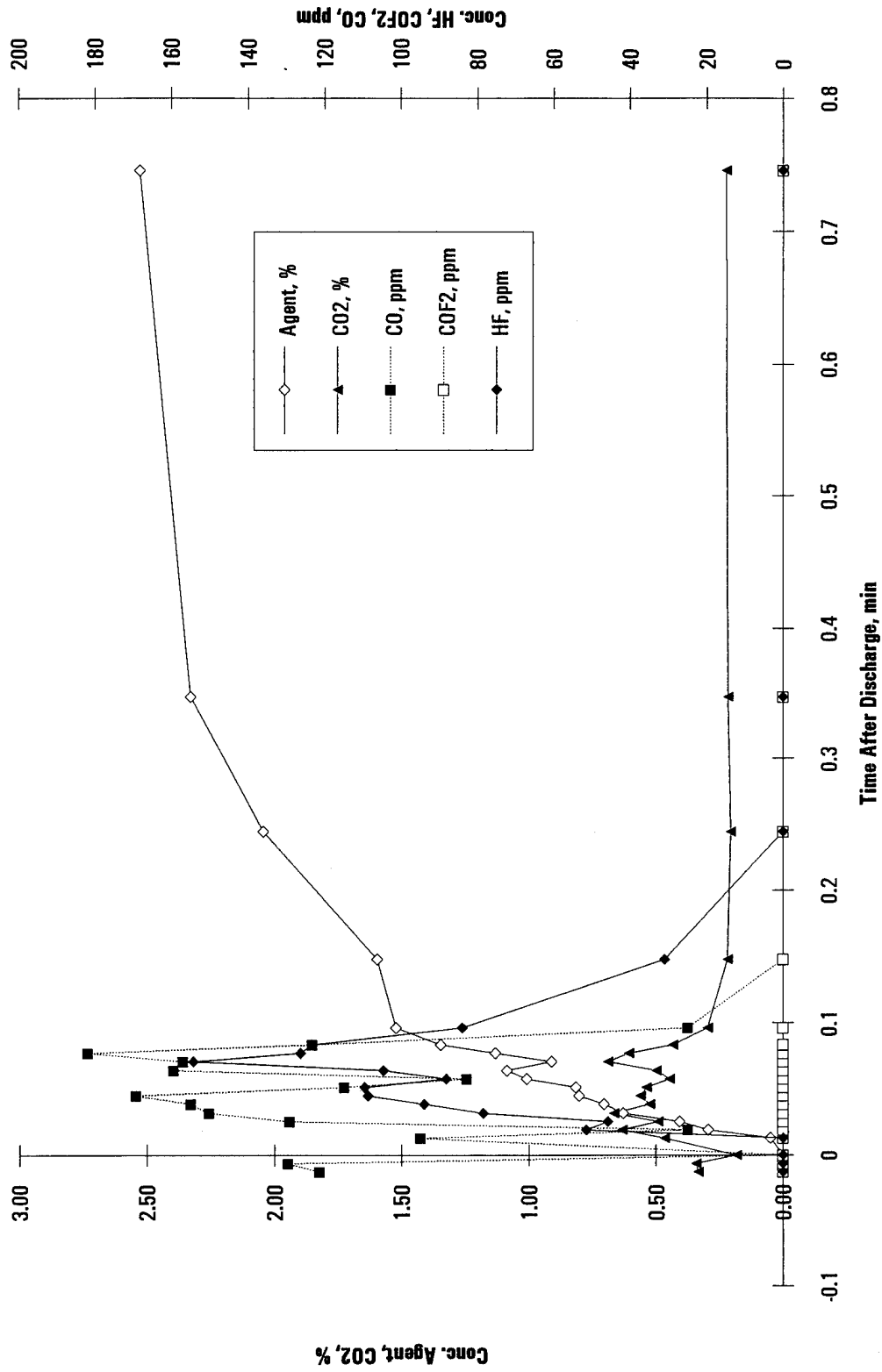


Figure A-1. Agent and Emission Concentrations.

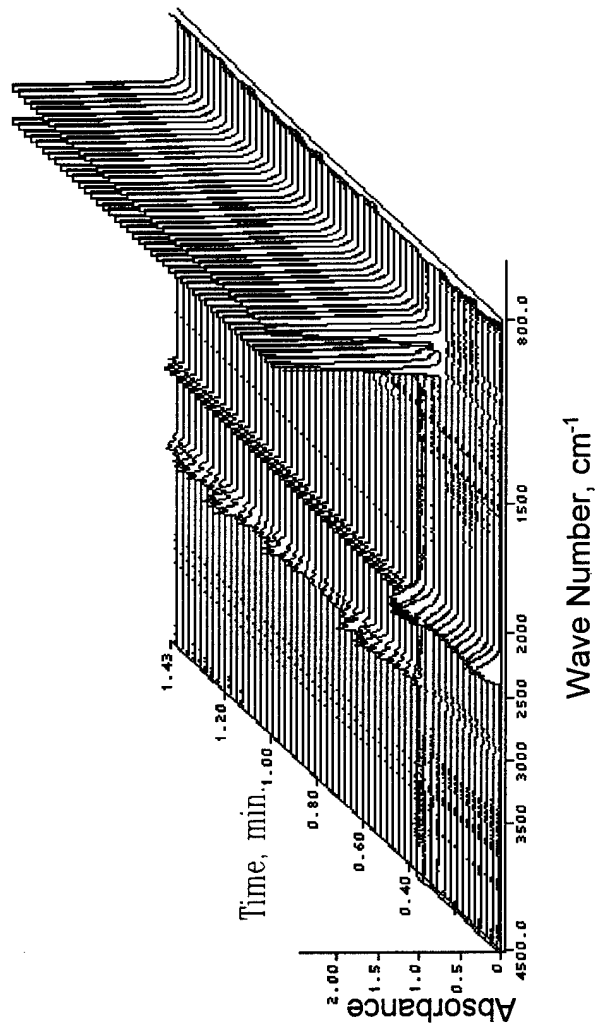


Figure A-2. Overall TRIR Plot.

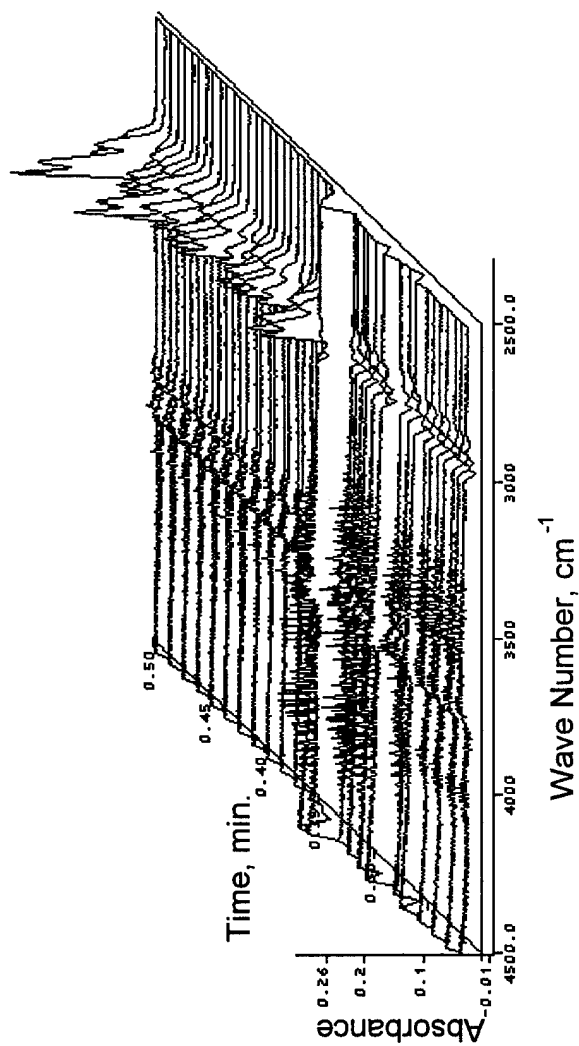


Figure A-3. TRIR Plot, 4500 - 2500 cm⁻¹.

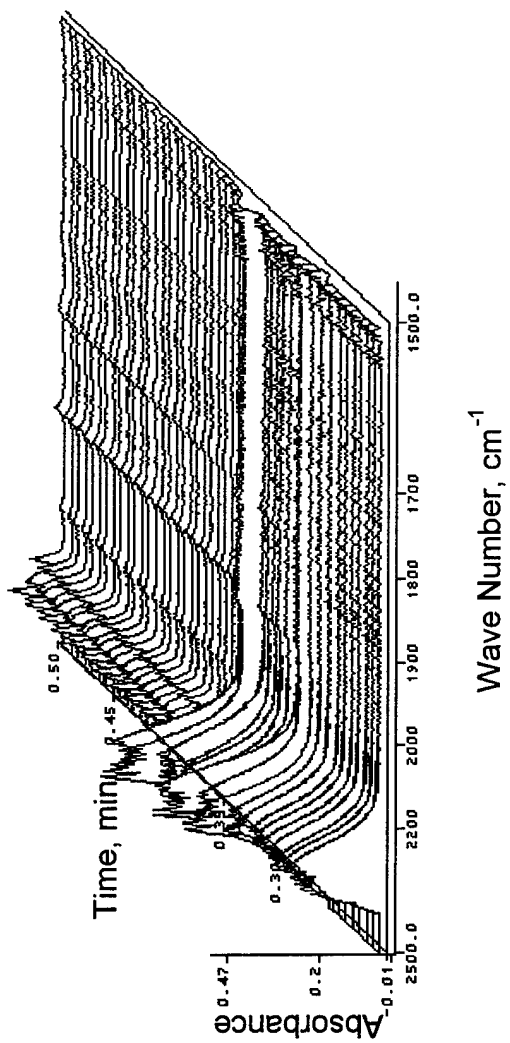


Figure A-4. TRIR Plot, 2500 - 1500 cm⁻¹.

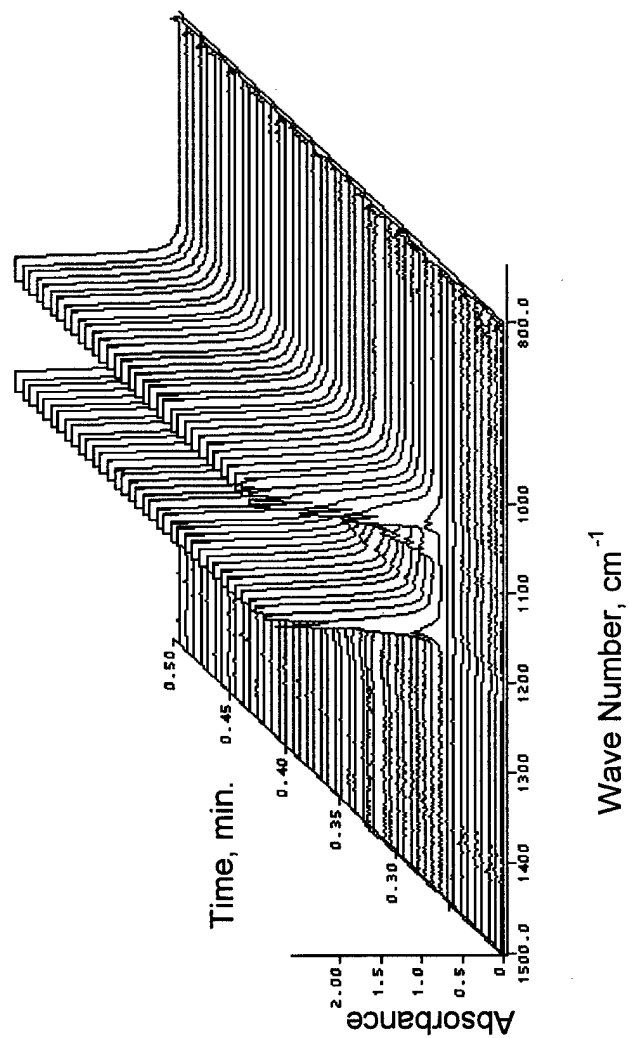


Figure A-5. TRIR Plot, 1500 - 800 cm⁻¹

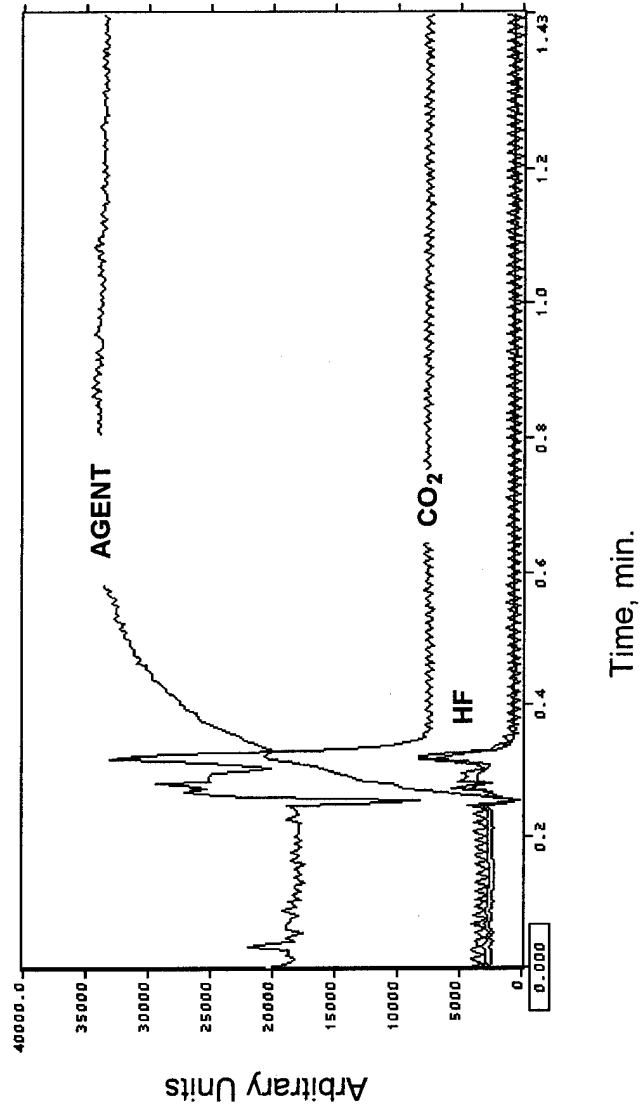


Figure A-6. Relative Concentrations.

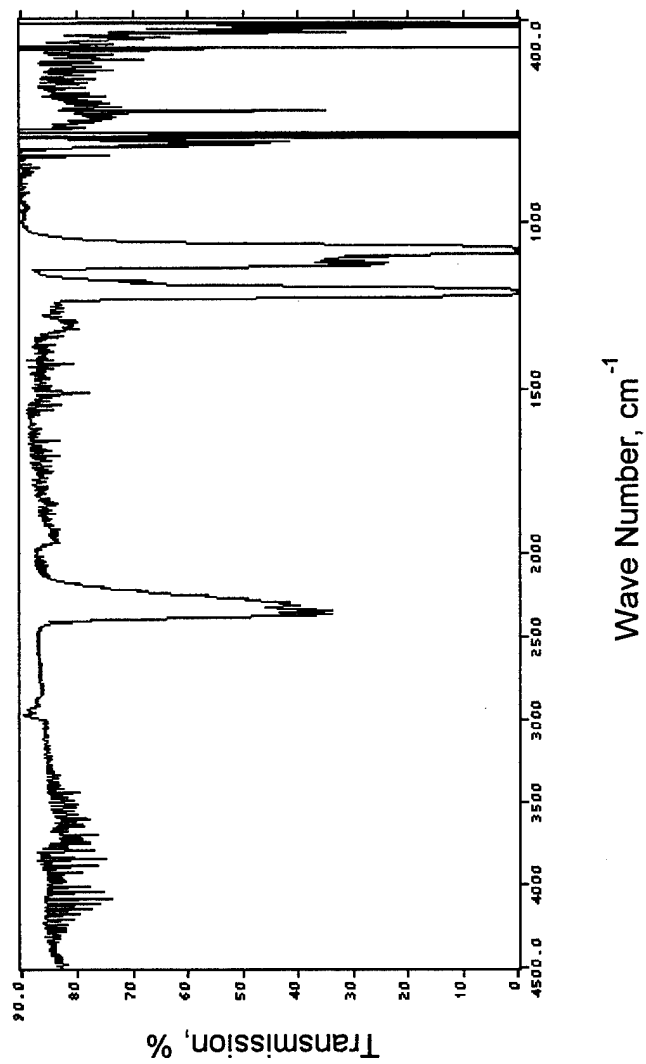


Figure A-7. Typical Spectrum During Extinguishment, $t = 0.0643$ min.

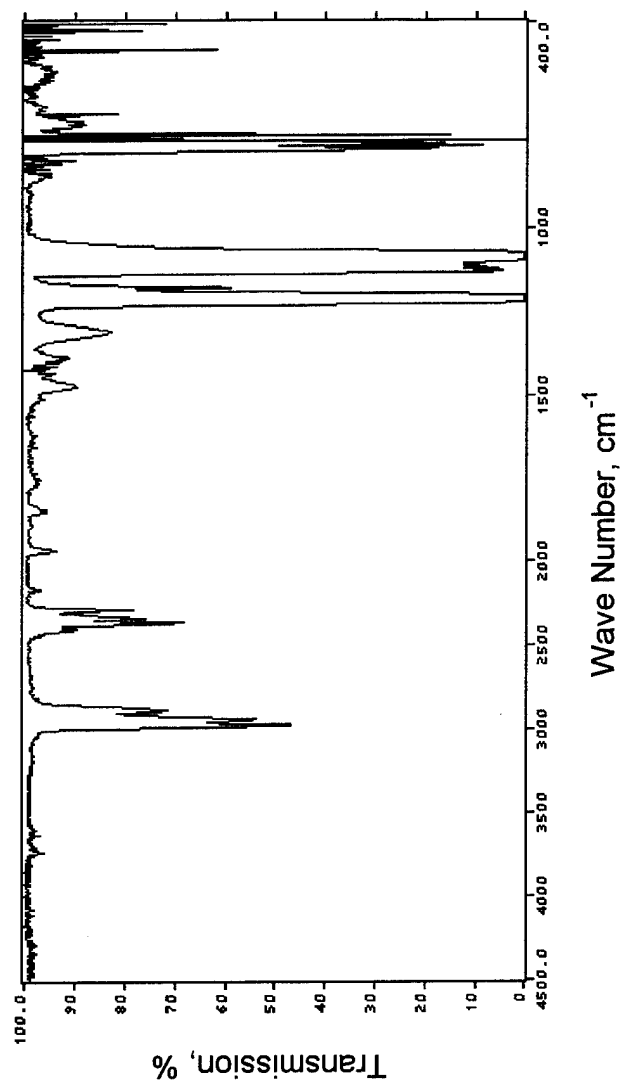


Figure A-8. Typical Spectrum After Extinguishment and Mixing, $t = 0.3473$ min.

TABLE A-2. TIME RESOLVED INFRARED (TRIR) SPECTROSCOPY.

Agent	HCF3	Weight	35.1 g.	Concentration	7.90%
Fire	.69 Cu Cap	Nozzle	Sprayco 1/4N -2	Pressure	600 lb/in. ²
Sampling	insitu	Pathlength	175mm	Resolution	2 cm ⁻¹

Notes

Quantitative Data

Concentrations							
Time		Time Rel. Discharge	Agent, %	HF, ppm	CO2, %	CO, ppm	COF2, ppm
Absolute							
0.232		-0.0129	0.00	0.00	0.31	0.00	0.00
0.2385		-0.0064	0.00	0.00	0.31	0.00	0.00
0.2449		0	0.00	0.00	0.33	0.00	0.00
0.2513		0.0064	0.00	0.00	0.19	0.00	0.00
0.2578		0.0129	0.00	0.00	0.15	0.00	0.00
0.2642		0.0183	0.41	0.00	0.22	0.00	0.00
0.2771		0.0322	1.15	28.52	0.30	0.00	0.00
0.29		0.0451	1.92	81.54	0.33	0.00	0.00
0.3029		0.058	2.49	102.05	0.35	0.00	0.00
0.3222		0.0773	3.57	133.14	0.35	25.03	0.00
0.3415		0.0866	4.00	141.19	0.41	25.03	3.71
0.3607		0.1158	4.84	318.24	0.51	25.03	4.79
0.3865		0.1418	6.21	182.19	0.38	25.03	0.00
0.4316		0.1867	8.96	278.34	0.44	58.04	5.01
0.4702		0.2253	7.14	488.37	0.73	93.06	8.45
0.4766		0.2317	8.37	322.85	0.37	15.91	4.22
0.496		0.2511	8.45	112.28	0.30	0.00	2.20
0.6955		0.4506	10.48	106.55	0.30	0.00	1.73
0.9979		0.753	9.89	81.68	0.30	0.00	1.70
1.191		0.9461	9.86	77.18	0.31	0.00	1.72

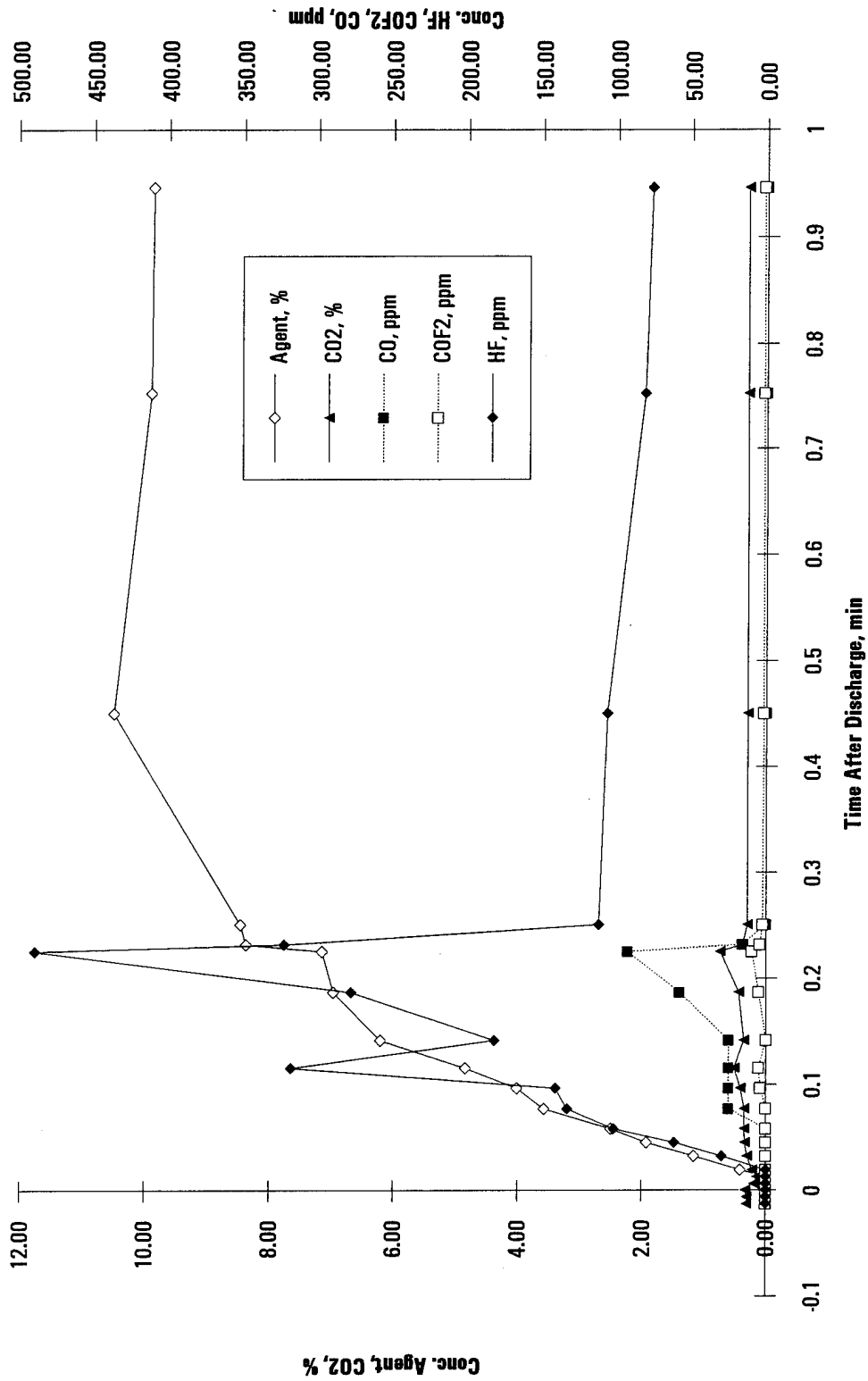


Figure A-9. Agent and Emission Concentrations.

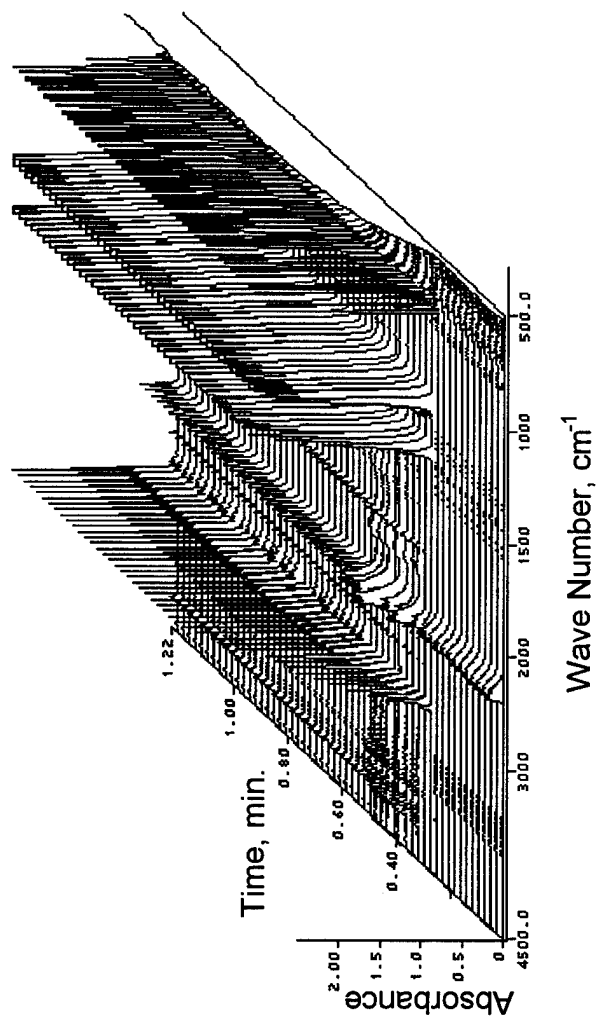


Figure A-10. Overall TRIR Plot.

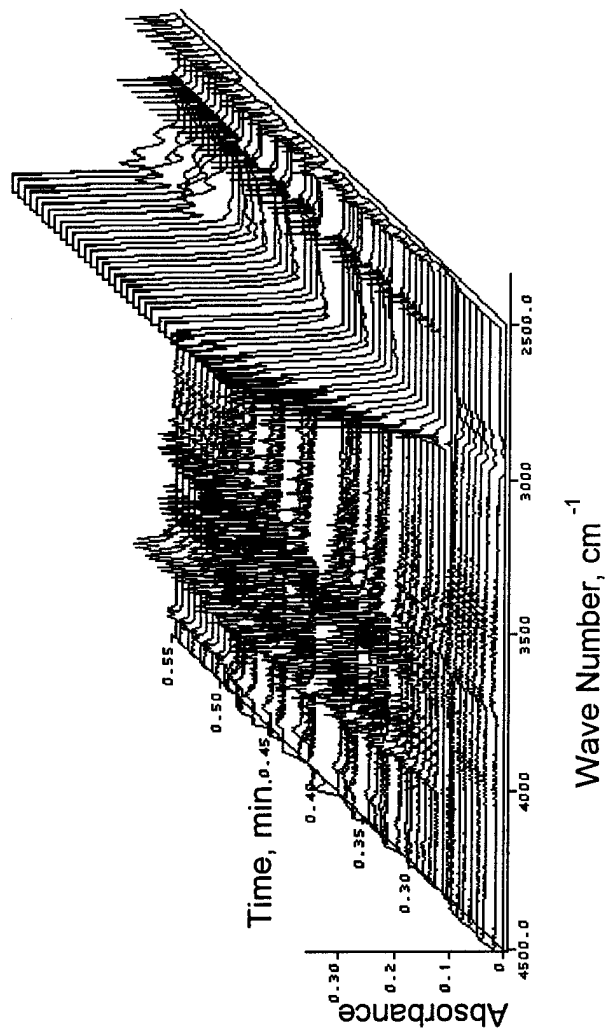


Figure A-11. TRIR Plot, 4500 - 2500 cm⁻¹.

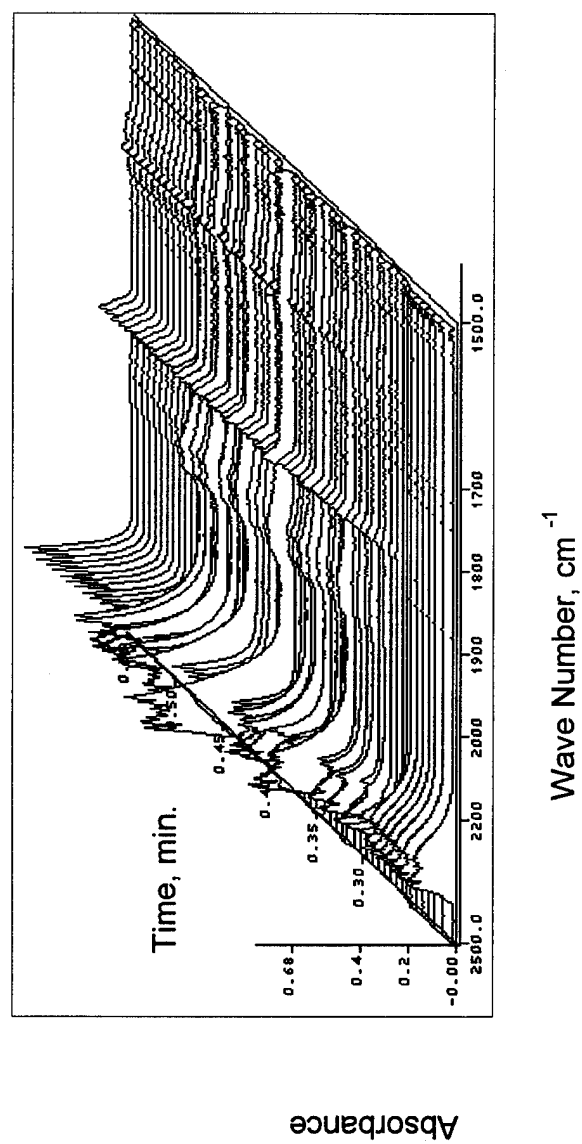


Figure A-12. TRIR Plot, 2500 - 1500 cm⁻¹.

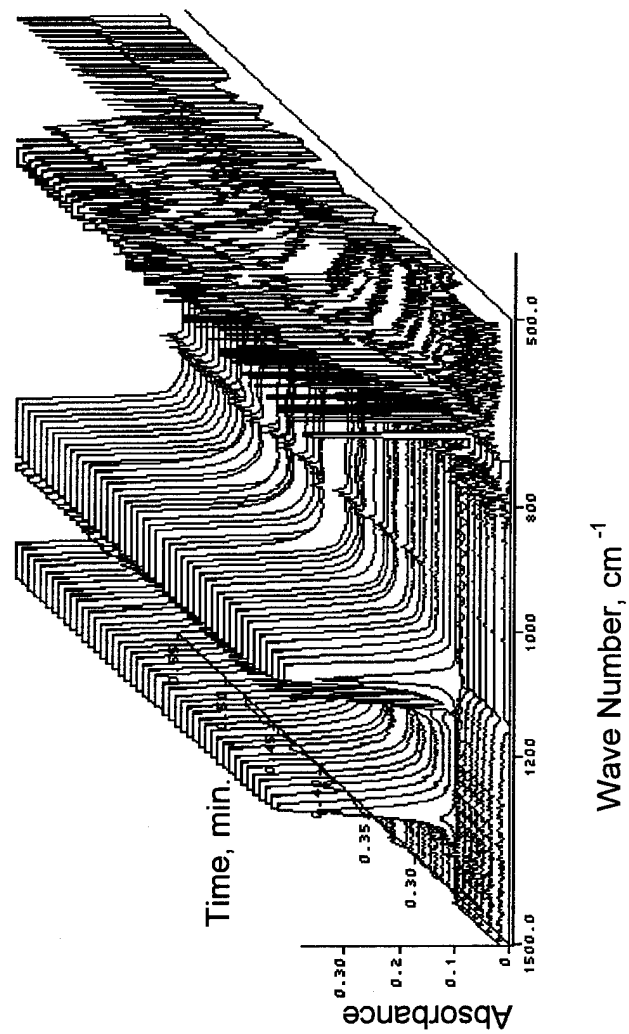


Figure A-13. TRIR Plot, 1500 - 500 cm⁻¹.

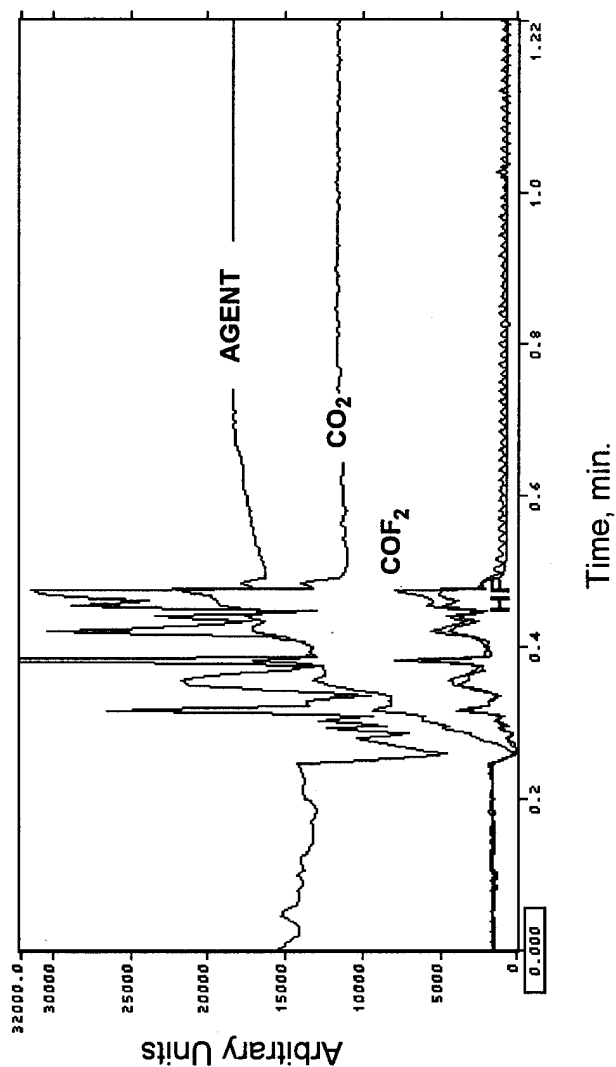


Figure A-14. Relative Concentrations.

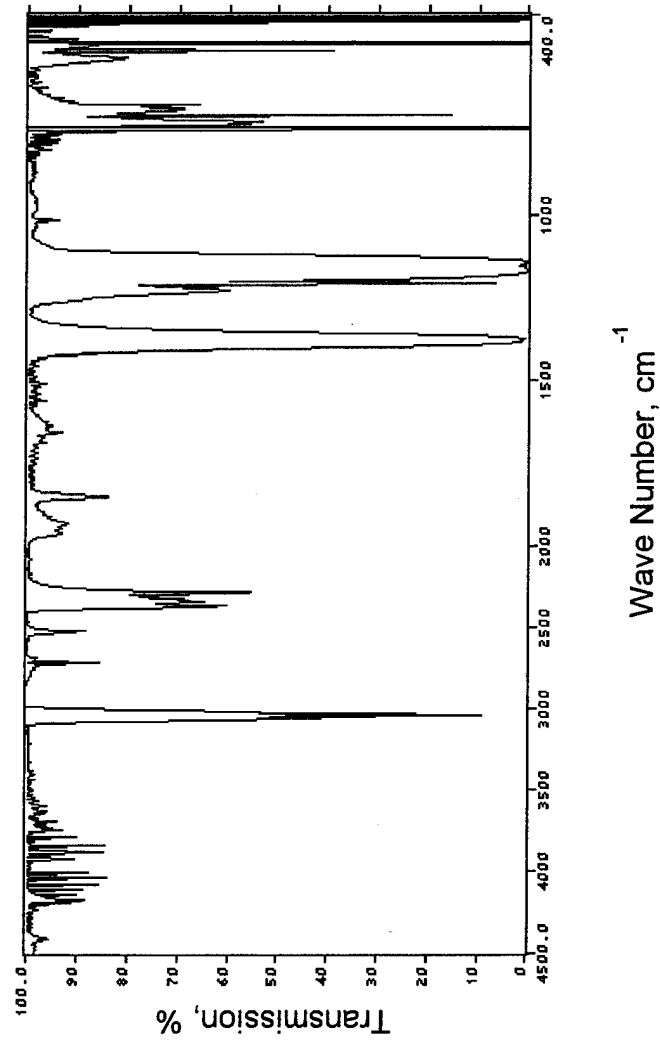


Figure A-15. Typical Spectrum During Extinguishment, $t = 0.1159$ min.

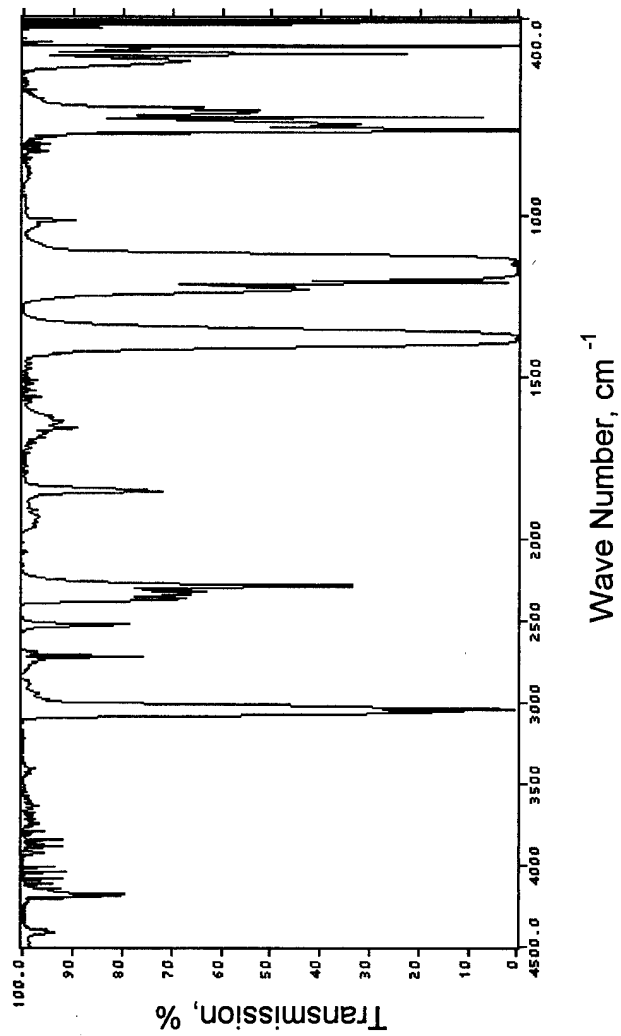


Figure A-16. Typical Spectrum After Extinguishment and Mixing, $t = 0.4377$ min.

TABLE A-3. TIME RESOLVED INFRARED (TRIR) SPECTROSCOPY.

Agent	227ea	Weight	49.9g	Concentration	4.75%
Fire	.69 Cu Cap	Nozzle	Sprayco 1/4N - 26	Pressure	200 lb/in. ²
Sampling	insitu	Pathlength	175mm	Resolution	2 cm ⁻¹
Notes					

Quantitative Data

Time Absolute	Time Rel. Discharge	Concentrations			
		Agent, %	HF, ppm	CO ₂ , %	COF ₂ , ppm
0.2334	-0.0193	-0.08	0.00	0.26	0.00
0.2527	0	0.01	0.00	0.16	0.00
0.2591	0.0064	0.95	5.17	0.34	0.00
0.2655	0.0128	1.80	72.79	0.31	20.13
0.272	0.0193	2.21	311.40	0.67	93.03
0.2785	0.0258	2.98	125.72	0.40	54.61
0.2849	0.0322	3.26	197.55	0.37	41.76
0.2913	0.0386	3.37	131.97	0.39	46.08
0.2978	0.0451	3.63	220.17	0.49	77.52
0.3043	0.0516	4.53	78.12	0.26	0.00
0.5938	0.3411	5.59	2.62	0.21	0.00
0.7998	0.5471	5.49	2.40	0.21	0.00

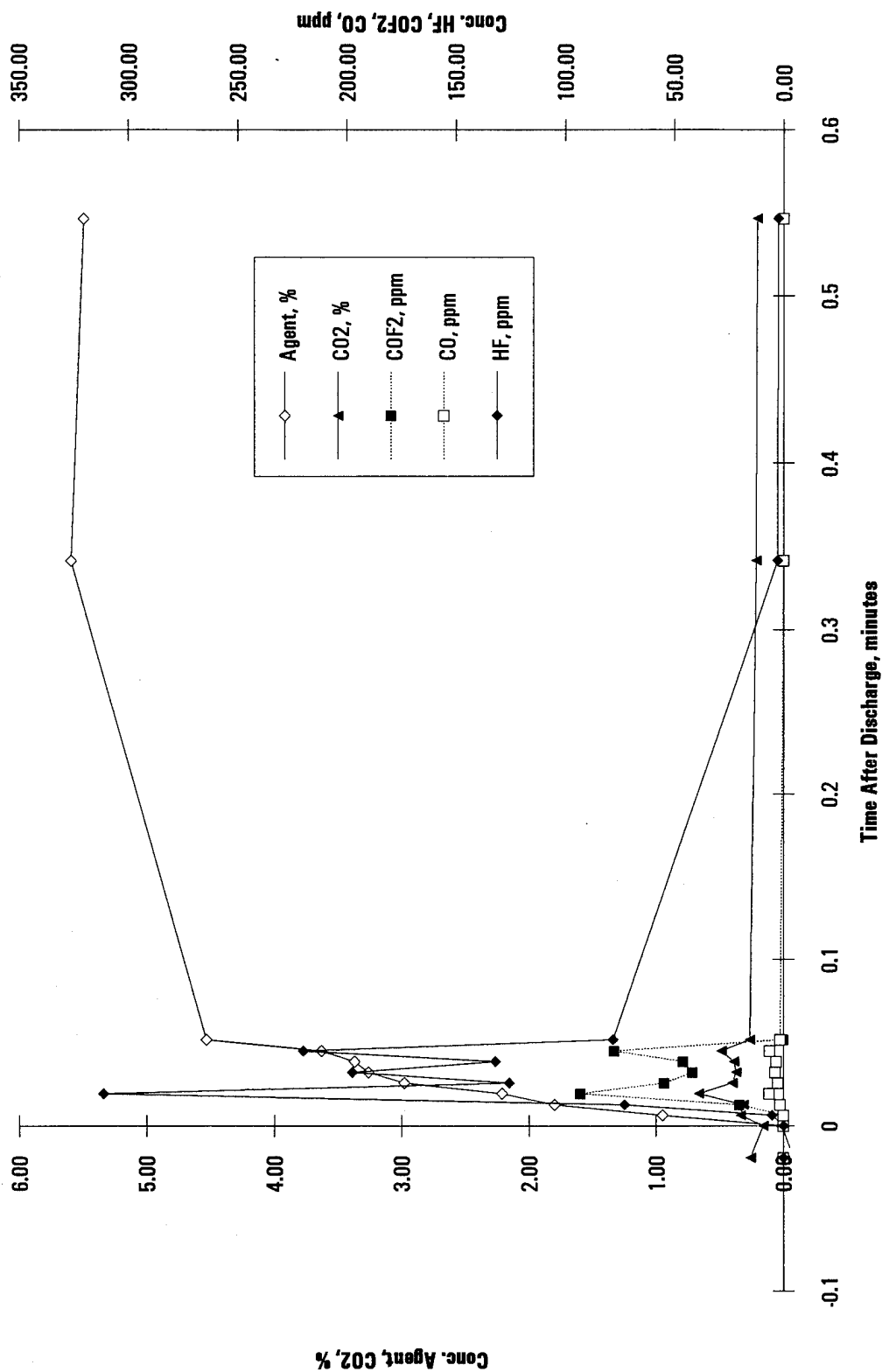


Figure A-17. Agent and Emission Concentrations.

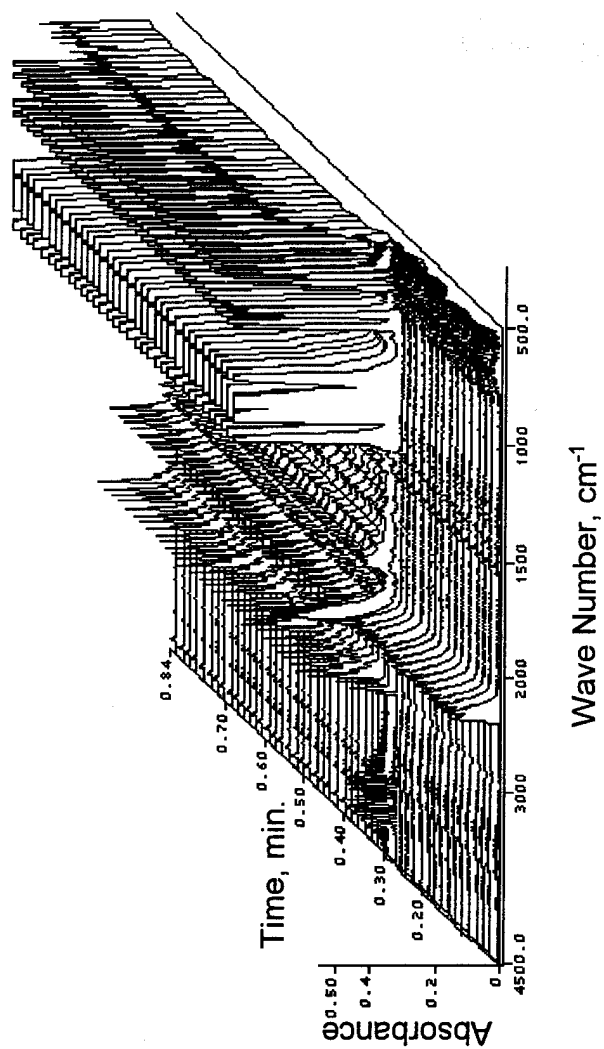


Figure A-18. Overall TRIR Plot.

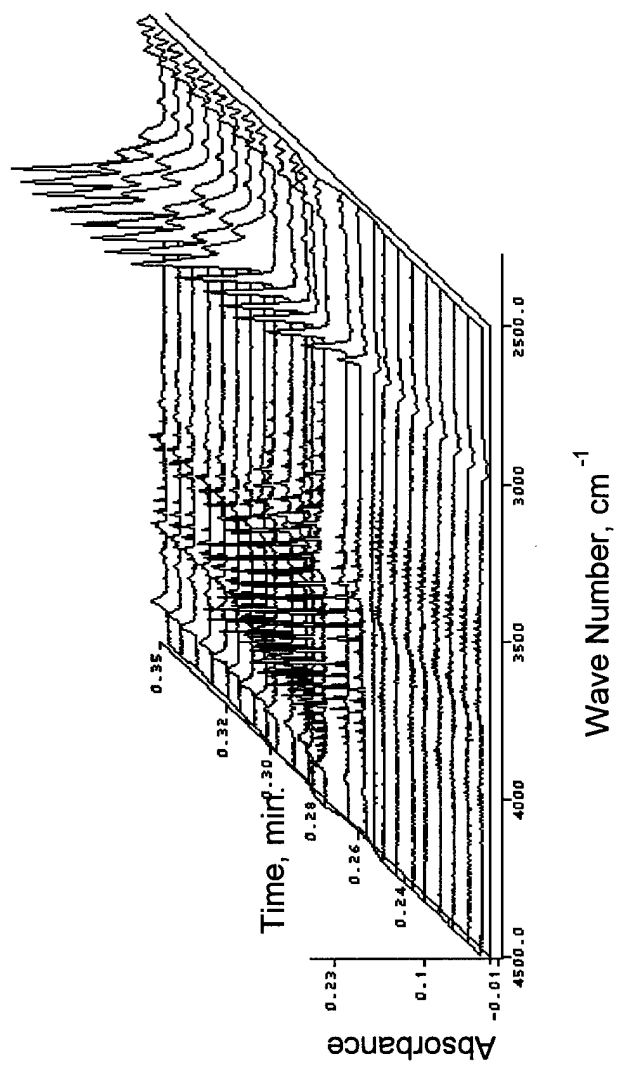


Figure A-19. TRIR Plot, 4500 - 2500 cm⁻¹.

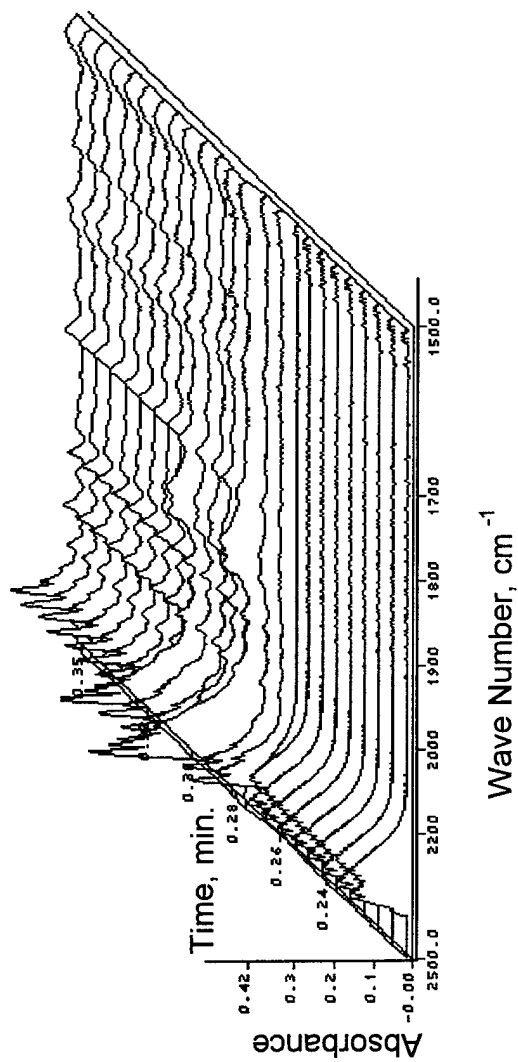


Figure A-20. TRIR Plot, 2500 - 1500 cm⁻¹.

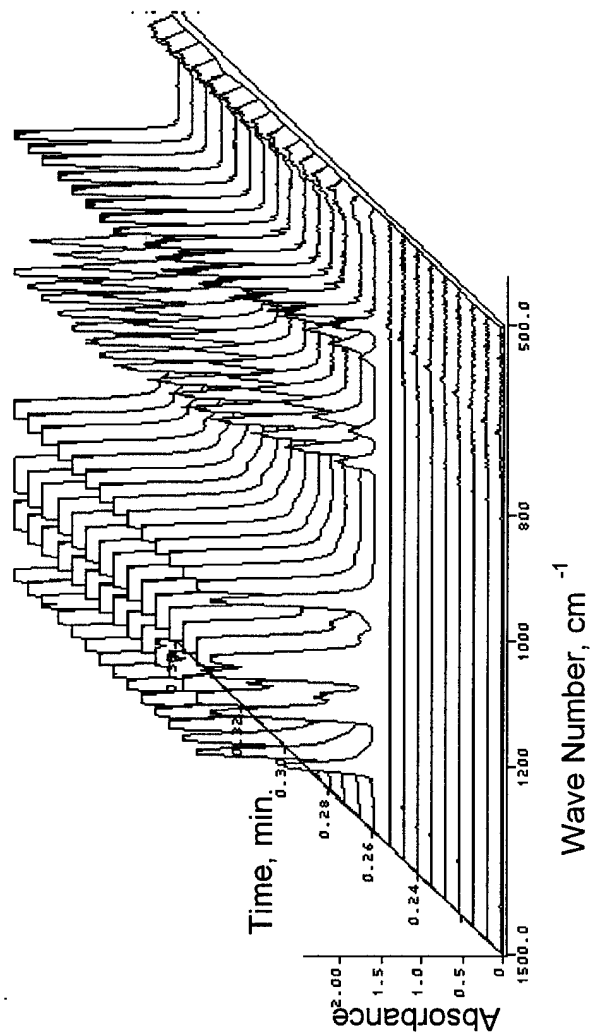


Figure A-21. TRIR Plot, 1500 - 500 cm⁻¹.

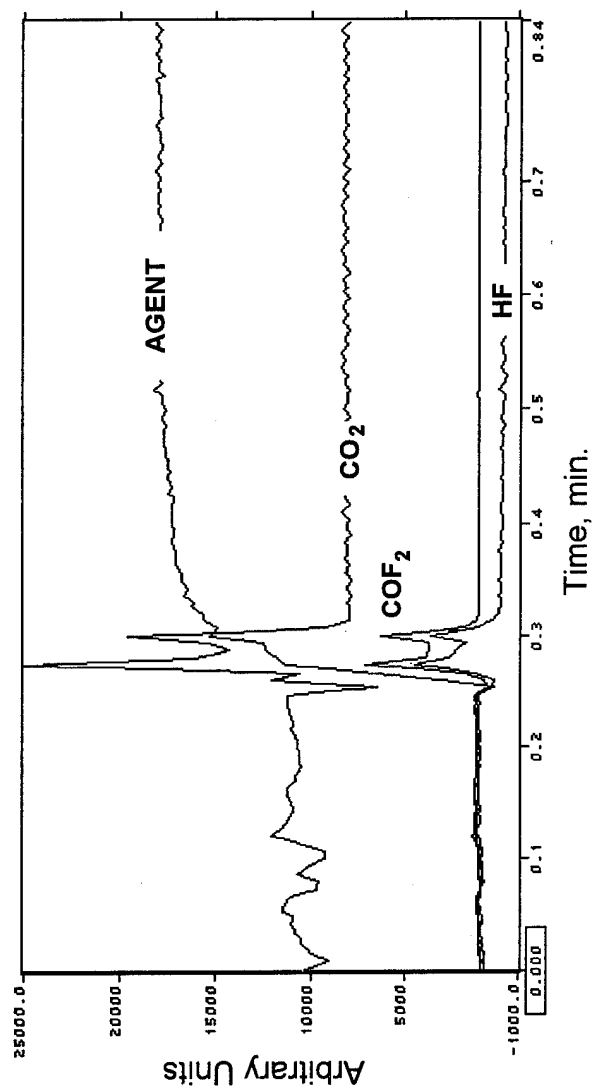


Figure A-22. Relative Concentrations.

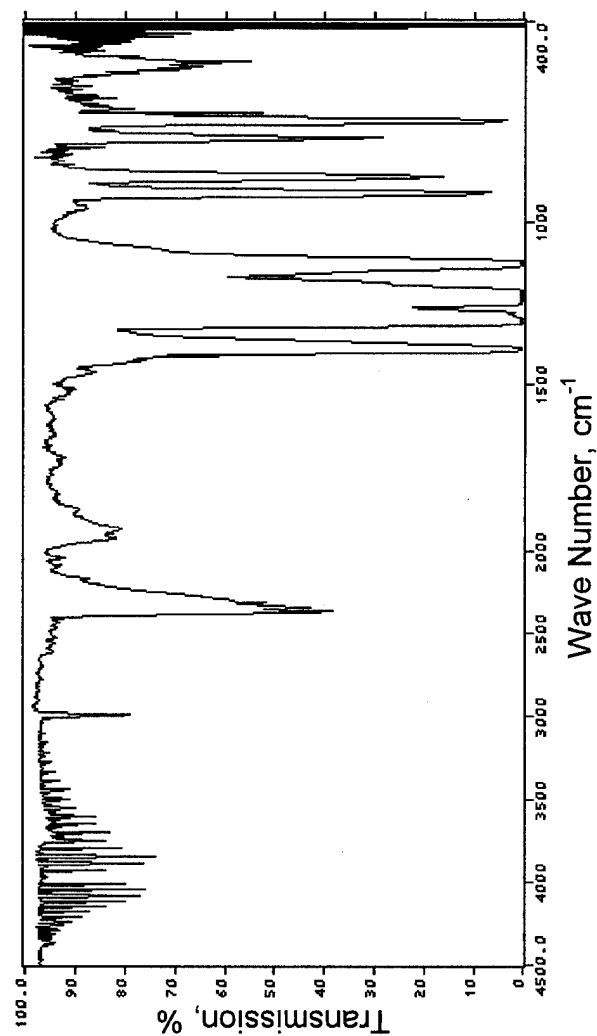


Figure A-23. Typical Spectrum During Extinguishment, $t = 0.0193$ min.

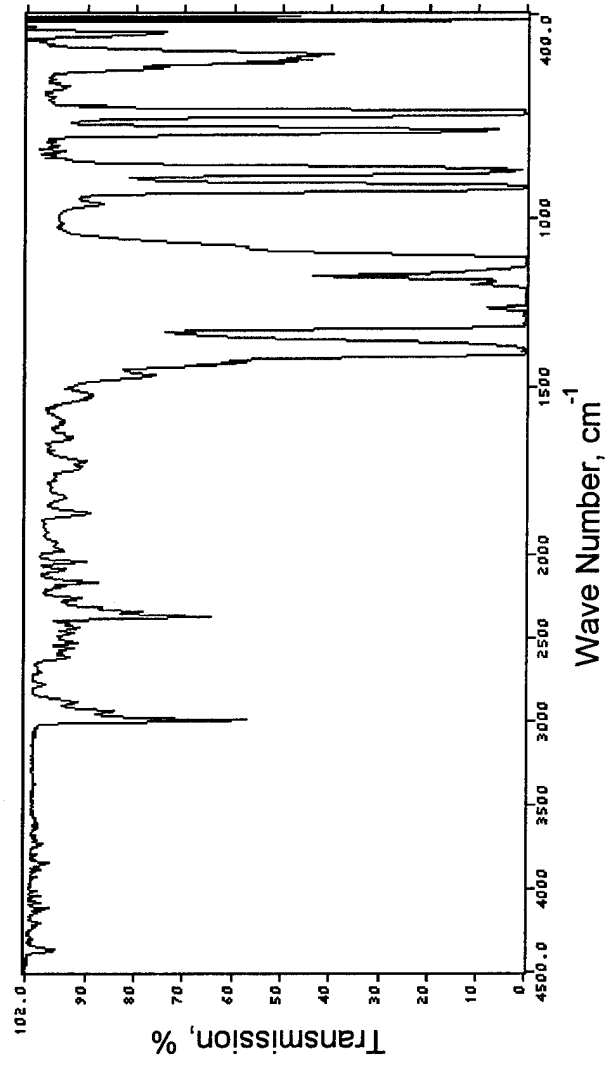


Figure A-24. Typical Spectrum After Extinguishment and Mixing, $t = 0.5471$ min.

TABLE A-4. TIME RESOLVED INFRARED (TRIR) SPECTROSCOPY.

Agent	FC 3-1-10	Weight	79.9 g.	Concentration	5.18%
Fire	0.69 Cu Cap	Nozzle	Sprayco 1/4N - 26	Pressure	200 lb/in. ²
Sampling	insitu	Pathlength	175mm	Resolution	2 cm ⁻¹

Notes Visual Extinguishment Time 4.3 seconds.

Quantitative Data

Time Absolute	Time Rel. Discharge	Concentrations				
		Agent, %	HF, ppm	CO2, %	CO, ppm	COF2, ppm
0.2255	0.0128	0.81	5.56	0.31	0.00	0.00
0.2449	0.0322	2.96	604.19	0.83	214.39	52.11
0.2963	0.0836	4.41	6.84	0.23	0.00	0.00
0.3994	0.1867	4.94	5.42	0.21	0.00	0.00
0.5989	0.3862	5.07	4.32	0.23	0.00	0.00

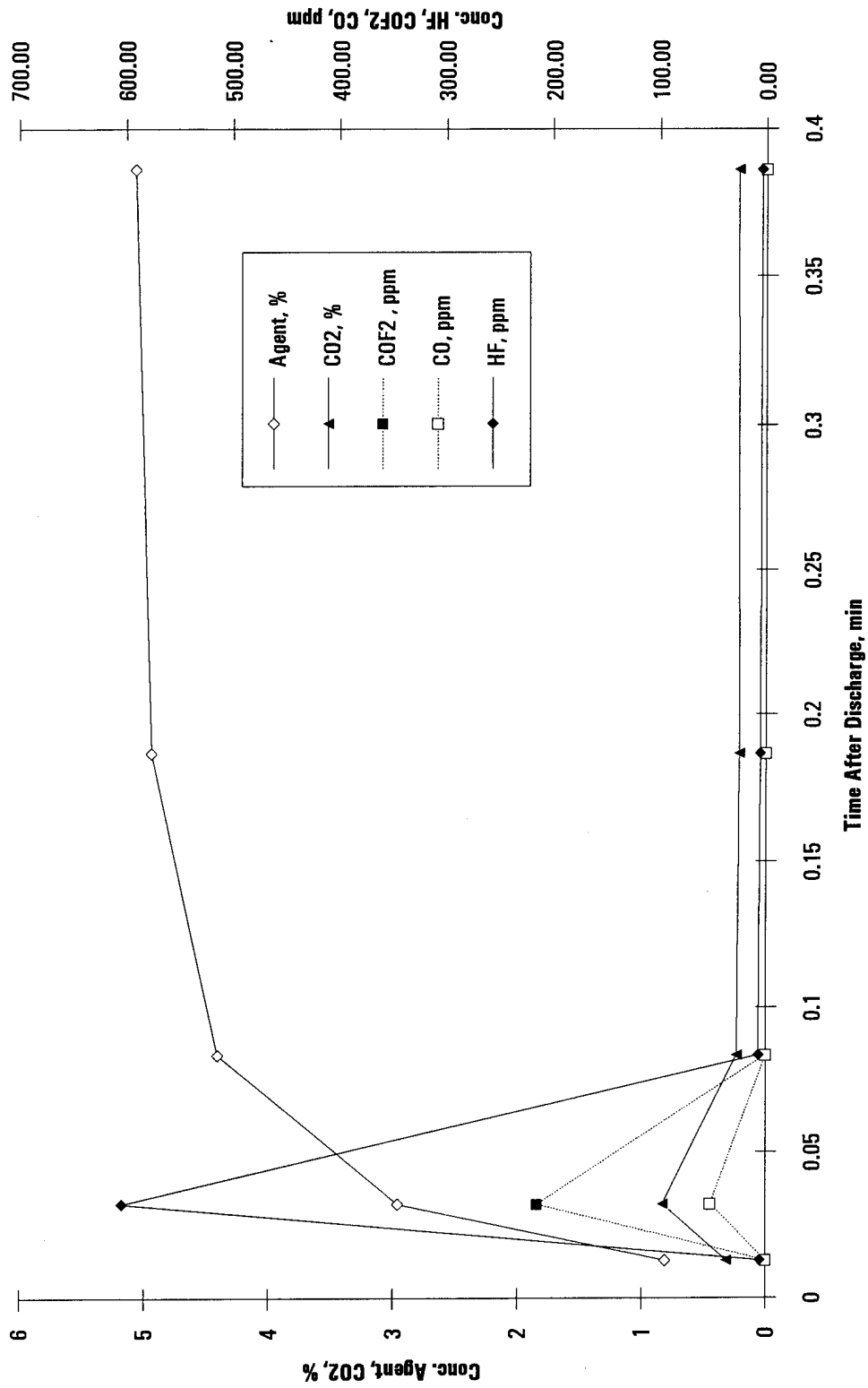


Figure A-25. Agent and Emission Concentrations.

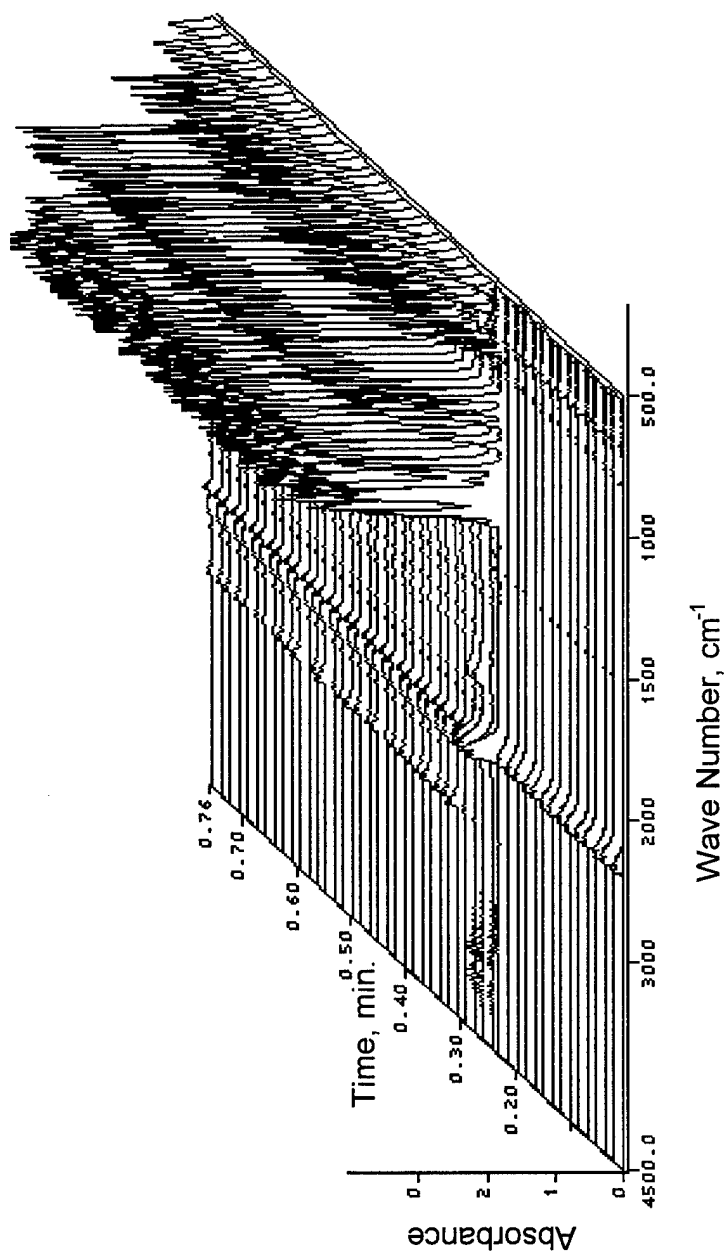


Figure A-26. Overall TRIR Plot.

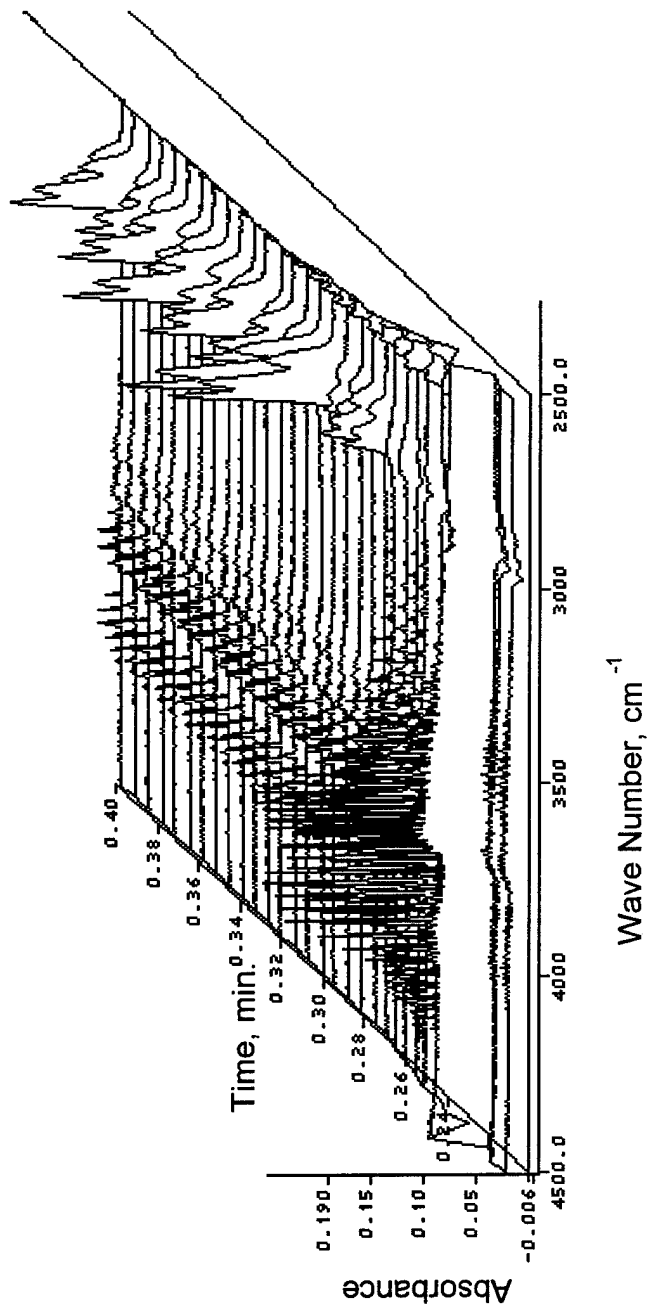


Figure A-27. TRIR Plot, 4500 - 2500 cm⁻¹.

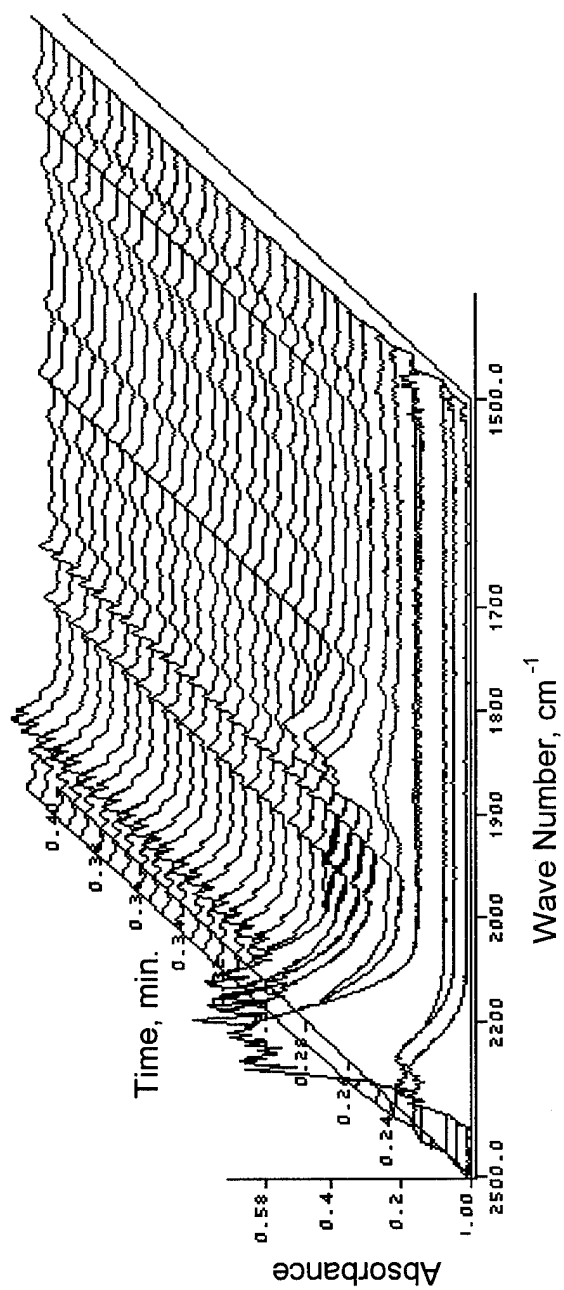


Figure A-28. TRIR Plot, 2500 - 1500 cm^{-1} .

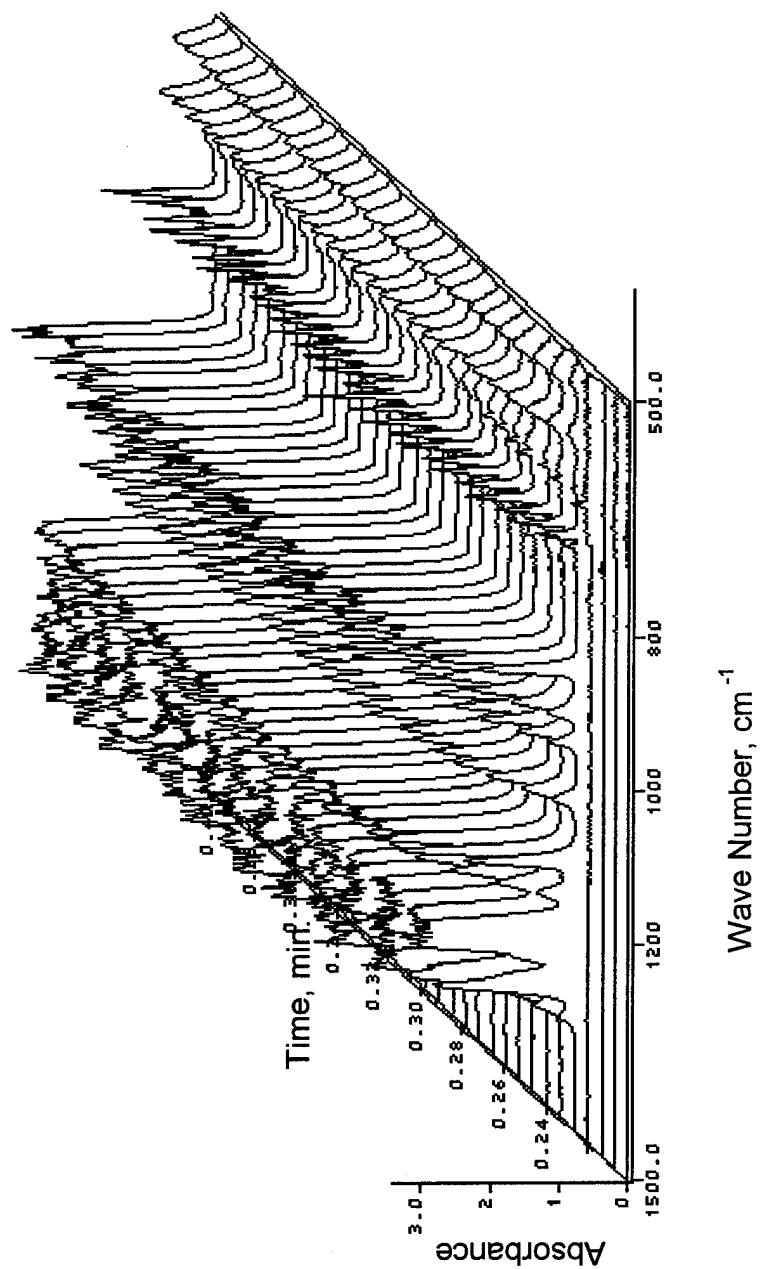


Figure A-29. TRIR Plot, 1500 - 500 cm^{-1} .

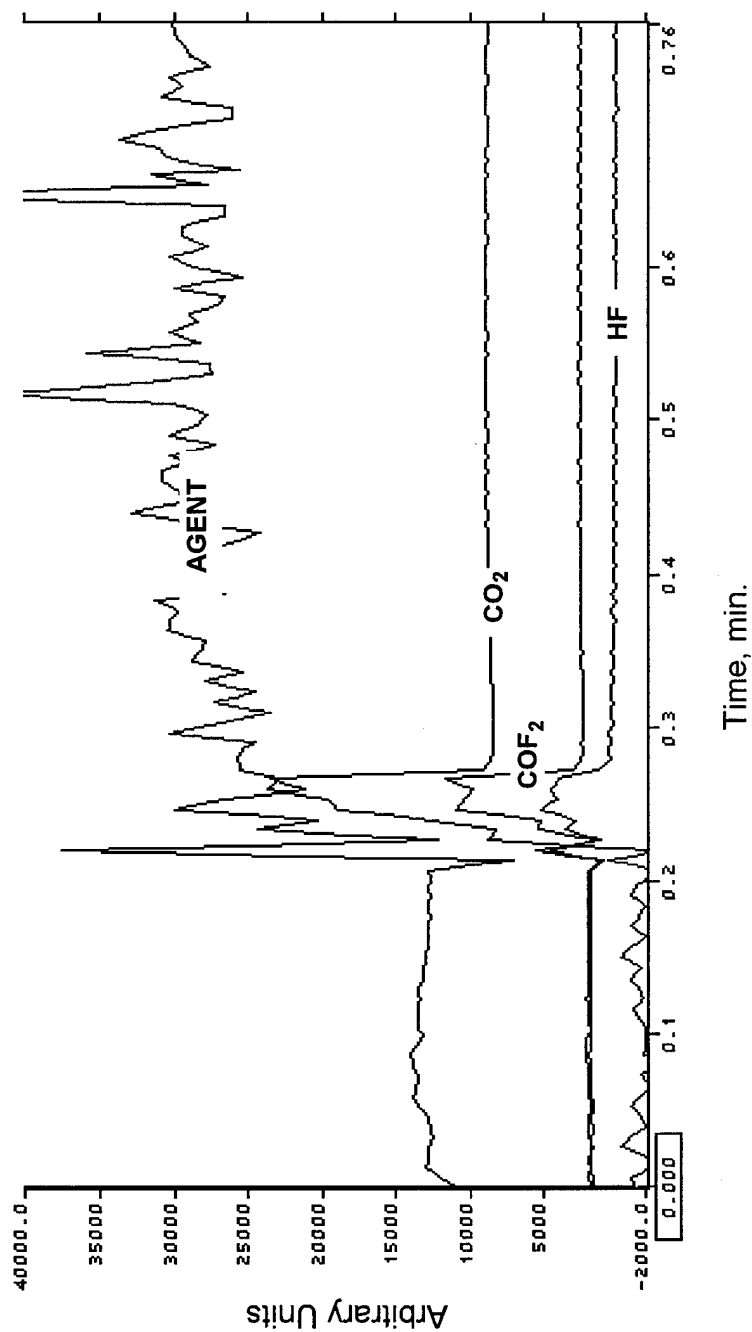


Figure A-30. Relative Concentrations.

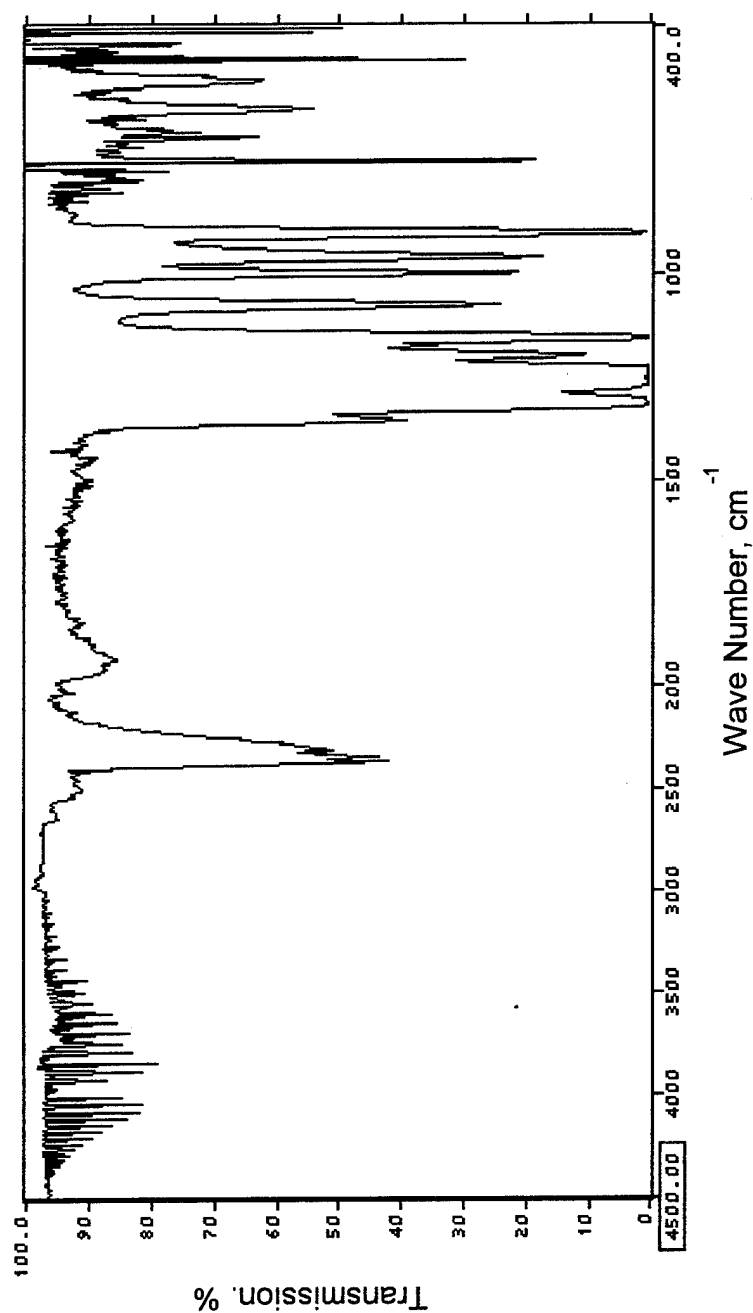


Figure 31. Typical Spectrum During Extinguishment, $t = 0.02$ min.

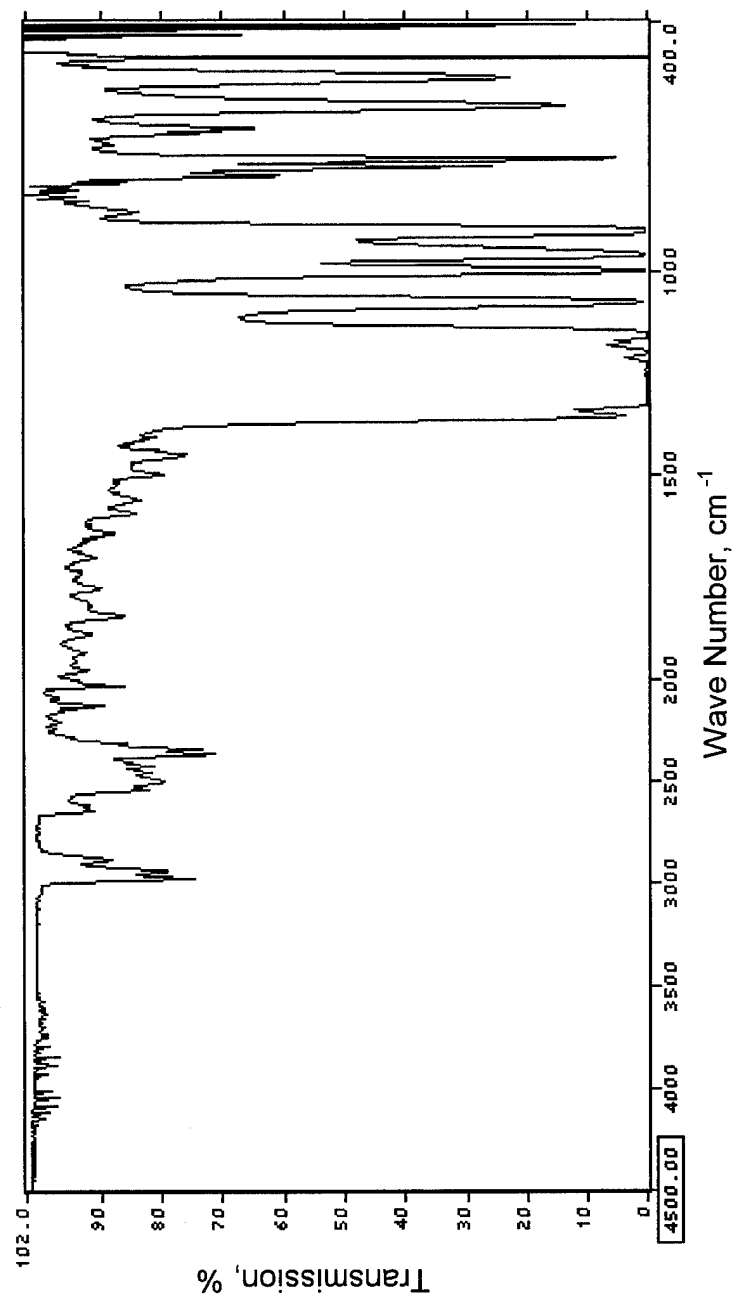


Figure 32. Typical Spectrum After Extinguishment and Mixing, $t = 0.386$ min.